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PHYSICS

A Journal of General and Applied Physics

The Journal of Rheology Now Combined with Physics

AT their meeting in December The American Physical Society and The Society of Rheology decided to combine the above two publications. The present issue is the first in which the combination has become effective. It is a "Rheology Issue" and will be followed periodically by others.

The primary reason for the combination was the need for economy but it has been apparent for some time that the articles in *The Journal of Rheology* would be generally appropriate for publication in a journal of the scope of *Physics*, dealing as the latter does with physics as an applied science.

The plan for the combined journal provides that every third issue of *Physics* shall be devoted to articles on rheological subjects. These "Rheology Issues" are to be prepared cooperatively by Dr. E. C. Bingham, Editor for The Society of Rheology, and Dr. John T. Tate, Editor of *Physics*.

No change will be made in the subscription price for *Physics* which is $7.00 for non-members and $5.00 for members of any of the member societies of the American Institute of Physics. The new dues of The Society of Rheology, $6.00, include a subscription to *Physics*.

The new plan, worked out by the two societies in cooperation through the Institute, is advantageous to all readers. The former subscribers to *Physics* will now receive a more fully rounded periodical at no additional charge. The former subscribers to *The Journal of Rheology* are assured of a continued medium for their field, which, because of the smallness of their numbers, would not be economically possible otherwise.

The Rheological Properties of Cement and Cement-Mortar-Stone[1]

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Beams of cement-stone and cement-mortar-stone with the ratio of cement to sand of 1 : 3 were allowed to bend under their own weight, the cross section of the beams being 2.27 cm square and the distance between the supports 76.1 cm. The deflections were determined at the central point between the supports by means of an Ames gauge reading to 1μ; the experiments were extended over a period of seven months. The curve of the deflection *vs.* time generally starts as a parabola having a vertical tangent but beyond a certain point the curve becomes linear. The slope of the curve is a measure of the *mobility* of the material. The parabolic curve is due largely to the hardening of chemical origin, resulting from the absorption of water, which causes a gradual decrease in the mobility, but to a smaller extent to an elastic after-effect. The mobility of the cement is much greater than that of the mortar and it decreases with the degree of curing. The *yield value* of the mortar is smaller than 45×10^5 dynes/cm^2 (65 lbs./in.^{2}) and the yield value of the cement was not perceptible with the apparatus used. For all practical purposes, cement-mortar-stone may be regarded as a solid of very low rigidity and cement-stone as a very viscous liquid. The curvature of the stress-strain curve, usually observed, is due to elastic after-effects arising from the fact that the experiments require time. The modulus of elasticity is smaller in the case of cement (230–260,000 kg/cm^2) than in the case of mortar (270–300,000 kg/cm^2); it increases with the number of curing days and approaches a constant value.

I.

CONCRETE and especially reinforced concrete have, during the short period since the beginning of this century, become most important as building materials. As a matter of fact, concrete and steel are the structural material of modern times and reinforced concrete is gradually replacing steel in many places. It is therefore the more astonishing that while the rheological phenomena connected with steel have found extensive scientific investigation and theoretical treatment—one can say that the imposing edifice of the classical theory of elasticity is mostly a theory of the elastic behavior of steel—the rheological investigation of reinforced or plain concrete has been very much neglected. To be sure there exists voluminous literature on experiments concerning the deformation and strength of reinforced concrete. These experiments however were made by engineers with the aim for the most part of obtaining results *which could immediately be applied in the design of reinforced concrete structures.* They therefore imitated in their experiments as much as possible the conditions under which the structural elements are required to act in the building structure and they had to be satisfied with empirical results for those different conditions, which could not be fully correlated.

The reason for this situation can easily be understood. Steel is a polycrystalline material but it can be considered macroscopically as if consisting of one homogeneous and isotropic phase and can therefore be treated according to the usual methods of the mechanics of continua. On the contrary, reinforced concrete consists macroscopically of four phases, i.e., cement, sand, stone and steel; it is heterogeneous and anisotropic and cannot be considered even as quasi-homogeneous or quasi-isotropic. The anisotropy is brought into the material through the steel which is inserted into reinforced concrete in the shape of rods, i.e., bodies one dimension of which far exceeds the other two. Concrete, which is an aggregation of the first three material constitu-

[1] The expressions "cement-stone" and "cement-mortar-stone" have been chosen in order to avoid the ambiguity in the expressions "cement" and "cement-mortar." The latter may mean either a semi-liquid paste (before setting) or a solid artificial stone (after setting); the former either a powder or a paste or likewise an artificial stone. This paper deals with cement and cement-mortar *after setting*, i.e., when they form artificial stones. Wherever in this paper the expressions "cement" and "mortar" are used, "cement-stone" and "cement-mortar-stone" respectively are meant.

ents, i.e., cement, sand and stone, can be considered as quasi-isotropic, but is heterogeneous because of the large size of the stones in the concrete. Mortar, i.e., cement and sand, is quasi-isotropic and can be treated to a first approximation as quasi-homogeneous. But cement itself, after setting, although it may contain water which is not chemically bound, is macroscopically isotropic and homogeneous. A scientific investigation therefore should not follow the way engineers have found necessary. It aims to understand the behavior of complicated systems from the behavior of its individual elements. A rheological investigation into the properties of reinforced concrete should therefore take up the study of steel and concrete separately, and when their properties are known, consider reinforced concrete as a heterogeneous and anisotropic mechanical two-phase system consisting of both. But even concrete has to be treated similarly. Its properties are to be derived from the known properties of mortar and stone after both have been studied separately.

II.

This procedure is the more important as recent engineering investigations have led to the observation of startling phenomena in the behavior of reinforced concrete, *viz.*, its plastic yielding. We may refer here to the investigations of O. Faber.[2] When Faber first presented the results of his observations before the Institution of Civil Engineers of Great Britain and the Royal Institute of British Architects it came to the engineers and architects as a surprise to learn that reinforced concrete structures may yield plastically under a load which is generally considered as safe in good practice. Another interesting paper has recently appeared[3] on the plastic flow in concrete-arches. Here the author has gone beyond the more qualitative reasoning of Faber and proposed as the law for the plastic yield of concrete

$$e_p = a p^b t^c, \tag{1}$$

where e_p is the plastic deformation, p is the unit stress, t is the time and a, b and c are constants. Apart from the objections which can generally be raised against laws of this type (power-laws),[4] one would arrive at the conclusion that the yield continuously increases without reaching any equilibrium. On the contrary, Faber's experiments (made with reinforced beams) have shown that the yielding did not exceed a certain limit. Furthermore Eq. (1) does not show a yield value, which means that the concrete would yield under any stress whatever no matter how small. In the discussion to Straub's paper, I. H. Griffith therefore naturally raised the question, "Is concrete a viscous liquid or a plastic solid?" This question could not be answered on the basis of previous observations. Another question which the engineering profession considers controversial is the question of the validity of Hooke's law for concrete. It is generally considered that the deformations increase faster than the stresses and that the modulus for tension is slightly larger than the modulus for compression and a power-law

$$e = k p^m \tag{2}$$

(where e is the strain, p the stress and k and m are constants) was proposed by Bach[5] as early as 1888. On the other hand, F. R. McMillan of the Research Laboratory of the Portland Cement Association, maintains that Hooke's law applies up to normal working stresses and that the modulus of tension is equal to the modulus in compression.[6]

It is most likely that these contradictions are due to the fact that in the study of these phenomena too many variables are involved. Experiments carried out with reinforced concrete beams of large size can hardly lead to the separation of such influences as properties of the constituent materials, chemical changes, shrinkage, elastic after-effect, strain-hardening, etc.

In the present investigation the small-scale methods of physics and chemistry were therefore adopted and only one material (cement) or an aggregation of two (cement and sand) studied at a time. When the rheological properties of cement and cement-mortar are thoroughly known, there can be greater promise in attacking the compli-

[2] O. Faber, Proc. Inst. Civ. Eng. **225**, 28 (1928).

[3] L. G. Straub, Trans. Amer. Soc. Civ. Eng. **95**, 613 (1931).

[4] M. Reiner, Naturwiss. (1933). In print.

[5] C. Bach, Z. Ver. Deutsch. Ing. **32**, 193 (1888).

[6] Reference 2. Discussion.

cated rheological problems connected with concrete or reinforced concrete.

III.

It was decided to carry out in the first instance observations on the deformations of beams by bending. While torsion-experiments would be most desirable from the theoretical point of view because one single kind of stress (the shearing stress) has to be considered, torsion experiments require a comparatively complicated apparatus. Compression experiments, while requiring simple apparatus, are most undesirable from the theoretical point of view because of the known difficulties of excluding friction at the surfaces where the external forces are applied. Bending experiments can be made with simple apparatus and while they have the disadvantage as compared with the torsion of a complicated theory, they possess the advantage of providing information on compression and tension at the same time. Square cement and cement-mortar beams were cast in a steel mould 83.8 cm long and 2.27 cm square. The proportion of cement and water in the case of cement beams, of cement, sand and water in the case of mortar beams, the process of mixing, casting, etc., was exactly in accordance with the Standards of the Joint Committee, i.e., the paste for the cement beams was made up with 24 percent water, the mortar paste with 10.5 percent water. The cement used was Alpha[7] cement, the sand Standard Ottawa sand. The proportion was 1 : 3 by weight. The beams were kept moist in the form for 24 to 48 hours and then put under water in a tank for the number of days shown in Table I and then allowed to dry in the air at room temperature. For bending, the beams were placed on two steel knife-edge supports with a span of 76.1 cm which were firmly fixed to an I-beam. The deflections in the center of the beams were determined by means of an Ames gauge, reading to 0.0001 cm. The zero-reading of the gauge was so adjusted that the points A, B and C (see Fig. 1) were on a straight line. This was done by means of a rigid straight-edge. The whole apparatus was enclosed in a case with a glass-door at the front, which was later made tight, so as to exclude as much as possible the variations of temperature and moisture of the outer air. Calcium chloride was later placed in the box, because the importance of having the air as dry as possible became clear in the course of the experiments. There was room in the case, however, for three beams only and the others had to be kept on additional supports and transferred for measurement to the case. The beams rested first directly on the supports, but later special bronze plates were attached to some of them so as to ensure as far as possible that the beams came to rest at the same points when transferred for measurement and that the gauge likewise touched the same point (see Fig. 1). The mainspring of the gauge was removed and the remaining hair-spring was ordinarily kept down with a weight, so as not to counteract the bending of the beams, and the spring was thus released for taking readings only. For loading the beam a small table was placed on its top surface in the center. Table I gives particulars about the beams used in the experiments.

TABLE I. *Cement and cement-mortar beams.*

Beam	Material	Date of Cstg.	Immersing into water	Taking out of water	First straining	Curing days	Weight (g)	First reading of gauge ($\times 10^4$ cm)
1	Mortar	3/31	4/1	4/15	4/18	14		351
2	"	4/1	4/2	6/28	6/29	87		
3	Cement	4/4	4/5	6/28	4/8	84	904	535
4	Mortar	4/11	4/12	4/22	4/27	10		631
5	"	7/14	7/16	7/21	7/22	5	886	213
6	"	7/15	7/18	7/22	9/6	4		338
7	Cement	7/20	7/21	7/27	7/28	6	867	111

IV.

The following problems were dealt with in the experiments.

(1) **To determine the deflection of a mortar beam under its own weight as a function of time.**

When the beam is placed on the supports, the first reading gives a combination of an elastic deflection and a protrusion (or concavity) of the beam, the sides of which are naturally not perfectly plane. As it is too difficult to measure these minute unevennesses, both influences can only be separated by computing the elastic deflection of the beam from some elastic law. As Hooke's law is not taken as granted, this can only

[7] We are indebted to the Alpha Portland Cement Company for the supply of materials.

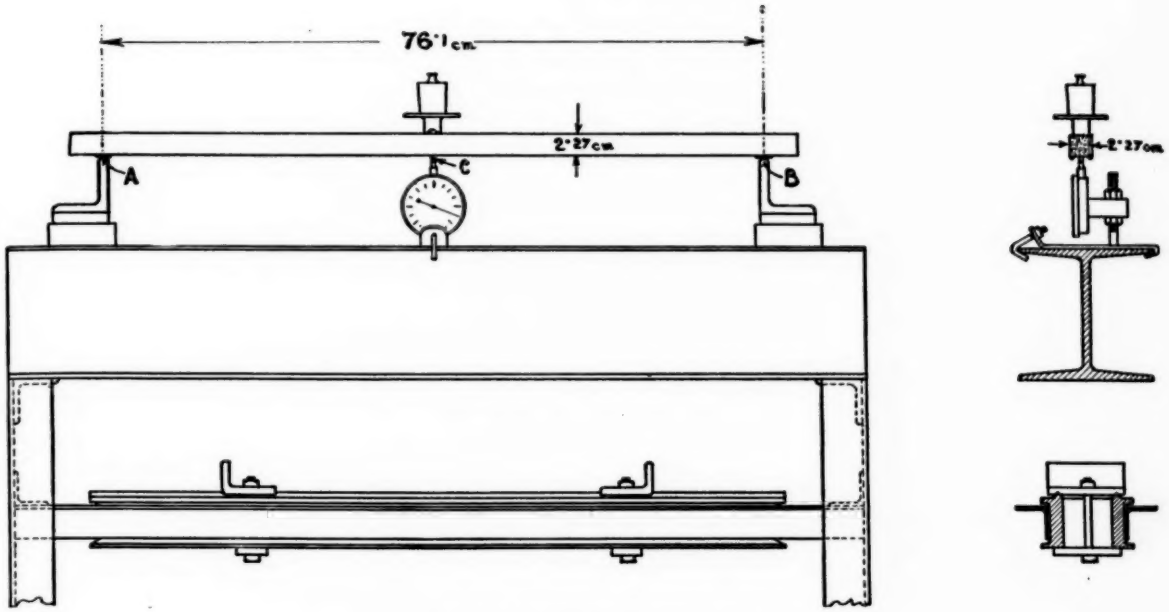

FIG. 1. Photograph of apparatus.

be done after such a law has been established from the experiments. In Fig. 2 the differences of readings over the first reading have therefore been plotted as ordinates against time as abscissae. From what has just been said there follows that these differences represent that part of the deflection which is dependent on time. As abscissae the number of days were plotted after the beam had been taken out of the water or what may be called the age of the beam. The abscissa where the deflection starts therefore represents the age at which the beam was first subjected to bending, Fig. 2. From curves 4/10 and 1/14 the following can be seen. The deflection curve starts as a parabola with vertical tangent and proceeds as such up to a certain point a after which the curve becomes a straight line. (The observational points are rather imperfectly placed on the curve. This is due to two reasons. When we put a beam over the gauge for measurement, it does not always rest on exactly the same points. The second reason is the hygroscopy of the mortar, which swells and shrinks according to the moisture content of the air.) According to the terminology introduced by Bingham we call "mobility" (μ) the measure of the rate with which a solid is continuously deformed after the yield value has been exceeded, where the yield value (ϑ) is the minimum shearing stress required to produce continuous deformation. Assuming for the sake of greater generalization that mortar is a solid (an assumption subject to examination and revision), the slope of the time-deflection curve is a function of μ, dependent on the dimensions of the beam, the loading, etc. We may call it the apparent mobility μ^1. Curves 10 and 14 therefore show that μ^1 first gradually decreases up to the point a and then becomes constant. For the beam with a larger number of curing days, μ^1 is smaller.

The decrease of μ^1 in the parabolic part may be due to one or a combination of the following causes: (a) elastic after-effect or (b) hardening. The latter may be either (α) strain or (β) chemical hardening. With regard to (a), it may be that after the initial elastic deflection has taken place at once, there is still a deflection going on which gradually decreases until it stops, the energy producing it not being dissipated but stored up, so that it can be regained. Such a strain is called elastic after-strain and the effect elastic after-effect. With regard to b, α it is well known that many polycrystalline materials show a hardening through strain. With regard to b, β it should be borne in mind that the mortar-paste hardens through the setting of the cement, i.e., the chemical binding of water. If the beam is taken out of the water and dried, some of the

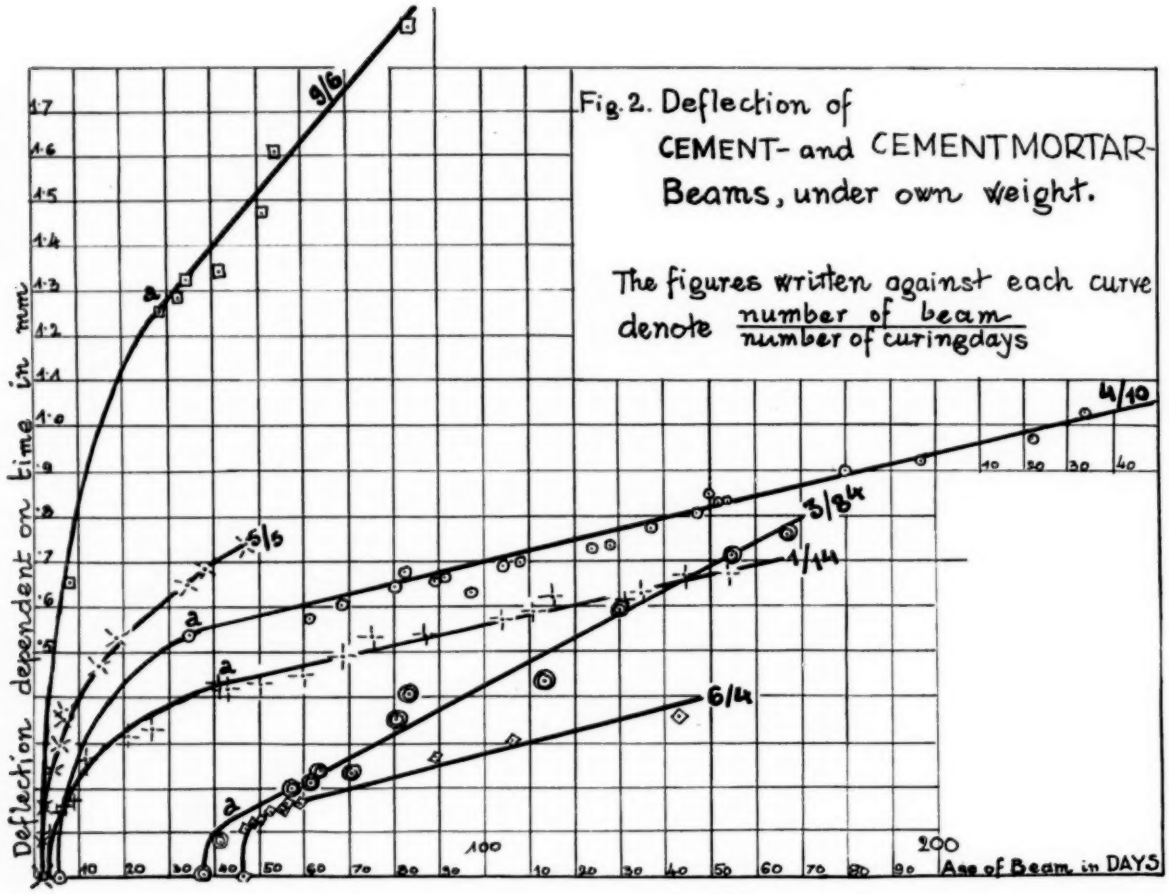

FIG. 2.

water will remain in the pores and the chemical process will continue. Besides this the mortar is very hygroscopic and takes on the moisture from the air and thereby also the chemical binding of water continues until an equilibrium is reached.

(2) To determine to what extent the causes enumerated under (a) and (b) contribute to the parabolic part of the curve.

To answer this question mortar beam 6/4 was allowed to dry for 46 days before being subjected to strain. From experience with beams 4/10 and 1/14 it was expected that during this period the chemical process had come to an equilibrium, or nearly so.

The deflection curve 6/4 shows a sharp parabolic bend at the beginning with a vertical tangent at the start and proceeds, after a few days only, as a straight line.

From this the following conclusions can be drawn: From curves 4/10 and 1/14 it can be seen that the decrease in apparent mobility after 46 days of age is very small. Such hardening as then exists is mainly chemical. If strain-hardening occurred, the curve would not become a straight line shortly hereafter, which means that all hardening has vanished, while the strain still increases. If therefore curve 6/4 at the same age shows a considerable deflection on being first strained, starting with an infinitely great apparent mobility which soon is lost to a large extent, this can only be interpreted as due to an elastic after-effect, which comes to an end after a few days.

The parabolic shape of the beginning of the curve is therefore due to the following causes. The first rapid deflection having a vertical tangent is due to an elastic after-effect which ceases after a short time. The deflection then proceeds on account of plastic flow only, with a

decreasing mobility due to chemical hardening. After the chemical process has come to an equilibrium, the mobility remains constant.

(3) These results were now checked on a beam the curing time of which came nearer to that of beam No. 6/4 than was the case with beams Nos. 1/14 and 4/10.

A mortar beam No. 5 with 5 curing days was available. It was subjected to strain one day after being taken out of the water. The deflection is shown in Fig. 2. While it had the same or slightly more curing than No. 6/4, its deflection was nevertheless much greater, due to the fact that its cement was not completely set. After becoming of the age No. 6/4 had, when first strained, the mobility was approximately the same in both beams. (Beam No. 5 was unfortunately broken inadvertently at the age of 47 days.)

(4) Is mortar a viscous liquid or a plastic solid?

The simplest way to obtain an answer to this question would be by decreasing the load under which the beam is deformed until the stresses reach the yield-value. The weight of the beam can of course not be reduced, but the span can be reduced and thereby also the stresses. The apparatus did not allow this procedure and therefore the following method was used: If we plot μ^1 as a function of the number of curing days we see that μ^1 decreases with increasing curing (see Fig. 3). If it is permitted to extrapolate the straight line, it would follow that a beam cured for 80 days or more would not flow under its own weight. This was checked and found to be correct with a beam (No. 2) cured for 87 days. In this beam the stresses due to the weight therefore do not reach the yield-value. We presume that also for the other beams with less curing, there are loads (smaller than their own weight) under which they would not flow.

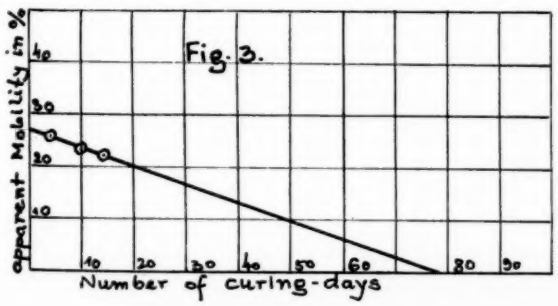

FIG. 3.

Mortar can therefore be regarded as a plastic solid, the yield-value of which depends on the number of curing days.

(5) Compare the behavior of cement with that of mortar.

Two beams with 6 (No. 9/6) and 84 (No. 3/84) curing days, respectively, were available. The beam No. 9/6 was first put under strain.

The deflection curve was of the same shape as the deflection curve for mortar beams, the mobility, however, being much greater. After 30 days μ^1 became constant with a comparatively great value. When the mobility of beam No. 9/6 had become constant, beam No. 3/84 was put under strain. This showed a very small, if any, elastic after-effect and nearly immediately showed a constant mobility. The chemical process had come to an equilibrium during the long curing period and no chemical hardening therefore occurred during strain.

By comparing cement curves 6 and 84 the following conclusion can be drawn: While chemical hardening during strain gradually decreases the mobility, this decrease will not proceed to such an extent as to reach the "stiffness" (reciprocal of "mobility") which can be attained through curing. This is confirmed also through a comparison of mortar beams of different curing periods.

(6) Is cement a viscous liquid or a plastic solid?

Considering that the apparent mobility of a cement-beam with as many as 84 curing days is about twice the apparent mobility of a mortar beam with only 4 curing days, and considering that the number of curing days in a concrete structure counts only in weeks, cement can be regarded for all practical purposes in structural engineering, in comparison to mortar, as a viscous liquid, i.e., it flows under the smallest stress of those orders of magnitudes as occur in structural engineering.

(7) Determination of the law of elasticity for cement and cement mortar.

Two kinds of experiments were made: (a) the beam was loaded with weights at its center which

were gradually increased to a maximum and likewise decreased to zero and gauge readings taken during this cycle as a function of the load; (b) the beam was loaded with a weight, the gauge read, the weight removed and the gauge read again. The procedure (b) was repeated with increasing loads until a maximum had been reached. These experiments were made with beams which had attained constant mobility. Each one of the experiments was completed in about one hour.

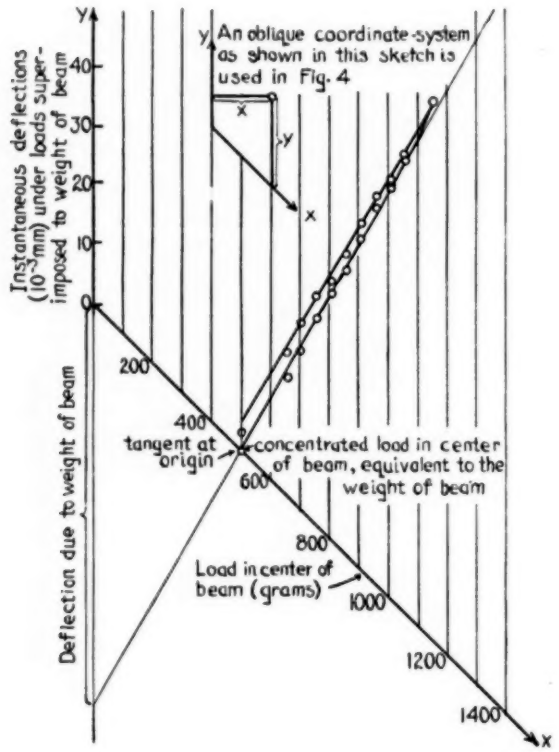
Instantaneous deflections (10^{-3}mm) under loads superimposed to weight of beam
Deflection due to weight of beam
An oblique coordinate-system as shown in this sketch is used in Fig. 4
tangent at origin
concentrated load in center of beam, equivalent to the weight of beam
Load in center of beam (grams)
0
200
400
600
800
1000
1200
1400

FIG. 4. Hysteresis-loop of beam 1/14.

If we take the gauge readings before the loading is started as zero, plotting of the readings against loads shows the following:

In case (a) the curve shows a hysteresis loop (see Fig. 4). Both its branches being bent upwards. The breadth of the loop at the origin was from 0.002 to 0.004 mm. The hysteresis loop can therefore not be due to plastic flow as the mobility was not nearly large enough to produce these yields in one hour. It can therefore be due only to an elastic after-effect.

In case (b) the curve is within observational error a straight line, its slope being nearly the same as the slope of the tangent at the origin of the curve of case (a).

From these experiments there follows:—The instantaneous elastic strain obeys Hooke's law. If the strain is measured while the load is gradually increased in time the strain-stress diagram will be curved and of parobolic shape with its convex side towards the stress-axis. This curvature is due to the elastic after-effect. The true instantaneous elasticity is given by the tangent to that curve at the origin.

While the exactness of the measurement was not great enough to substantiate definitely the following statement, it appears likely that the hysteresis loop was narrower in the case of cement than in the case of mortar, which would substantiate the conclusion drawn before that cement shows a smaller elastic after-effect than mortar.

(8) What is the relation of elasticity to the length of curing period?

From Table II it can be seen that the coefficient of elasticity (reciprocal of Young's modulus) is greater in the case of cement than in the case of mortar, that it decreases with increasing curing and tends to become constant.

TABLE II. *Coefficient of elasticity of cement and mortar beams.*

No. of beam	Material	No. of curing days	Observed slope dy_p/dp in 10^6 cm/g	ϵ in absolute units $\times 10^{15}$	ϵ^{-1} in kg/cm^2 $\times 10^{-3}$	Y_p cm
1	Mortar	14	13.9	3475	299	0.007
3	Cement	84	15.7	3925	265	0.008
4	Mortar	10	14.3	3575	291	0.007
5	"	5	15.2	3800	274	0.008
6	"	4	15.5	3975	268	0.008
9	Cement	6	18.1	4525	230	0.009

V.

The present investigation has therefore led to the following conclusion:

Cement on setting can be considered to resemble a viscous liquid. It either has no yield value at all, or else its yield value is negligible under conditions of curing time and state of

stress[8] which prevail in structural engineering. Its mobility is comparatively high; it depends on the curing time and age, decreasing with both.

On the contrary, mortar is probably a plastic solid.—The fact that an aggregation of loose grains (as e.g., sand) and a viscous liquid gives a plastic solid is well known to rheologists. Examples are moist clay, wet sand, etc. The binding forces producing the yield value are due to the solid friction between the grain-particles, to the surface tension and to the solidification of the liquid in molecular layers. The yield value of such a system is naturally not very great; e.g., we have found that the yield value of cement mortar under ordinary conditions of curing time is below 5 kg/cm².

After the yield value has been exceeded the mortar flows, as a result of the viscous flow of the cement in it, while the sand-particles slide over each other, the friction between them reducing the mobility of the cement.

The plastic properties of reinforced concrete or concrete in compression can now be easily understood. If we have a concrete in compression under ordinary stresses the yield value of the mortar between the stones, which form the coarse aggregate, is always exceeded. The concrete then yields as a whole until the stones touch each other, forming arches which carry the load. The plastic yielding then ceases, as the yield value of the natural stones is high and will usually not be exceeded. In the case of reinforced concrete, the steel will take the tension stresses and in the region of compression the conditions prevail as described above.

This answers the question why a concrete arch-bridge, as was pointed out by Vogt and Gilkey "does not deflect until it is flattened to the point of failure" (in any case in historical times) as would result from the formula (1) proposed by Straub. Continuous flow takes place in the *mortar* only and it is most likely that the structure will come to an equilibrium when the stones touch each other. Then the plastic yielding stops. As a matter of fact it has always been considered as good practice in concrete construction not to use more mortar than will just fill the interstices between the stones. In this case the plastic yielding will be small and will stop soon.

[8] The stresses in the beams were much below the usual working stresses, the maximum stress being about 5 kg/cm². See Appendix I.

VI.

With regard to the question of the law of elasticity we have to be careful in separating instantaneous elasticity from elastic after-effect, and in finding a definition for the former which will not be contradicted by observations. Cement is according to our investigations, a viscous liquid. We have nevertheless determined a coefficient of elasticity for it and have to say what is meant by the coefficient of elasticity of a liquid. The correct definition for this has already been given by Maxwell in his theory of relaxation and revived by Bingham.[9]

In the calculation of the coefficient of elasticity, the instantaneous strain at "zero-time" has to be taken into account and its relation to the stress determined. This will give the true elasticity, as shown in Section IV (7) above under (b). As a result of our investigation it follows that the elastic law, on the basis of this definition, is Hooke's law, as had been assumed by Maxwell and Bingham. Their definition and method can, however, also be applied in the case of a solid, as has been done here with the mortar beams.

If a body formed by a homogeneous system consisting of a solid and a liquid phase is stressed, the following will result: There will first be an instantaneous elastic deformation according to an average elasticity of the combined system. Then the liquid will start to flow and the body be deformed considerably more. This brings with it increased straining of the solid phase, to which the latter resists with elastic forces until its yield value is reached. To this elasticity, brought about by flow of the liquid phase in a liquid-solid system, is due the elastic after-effect. This is confirmed by our observations that cement which is microscopically homogeneous shows a small elastic after-effect, while mortar which is microscopically heterogeneous, consisting of a liquid and a solid phase shows a considerable elastic after-effect. At the same time the conclusion is justified that the deviations from Hooke's law are due to elastic after-effects. It is

[9] E. C. Bingham, Kolloid. Zeits. **47**, 1 (1929).

however admitted that this conclusion is not final because of the scarcity of data.

VII.

The results of our investigations have so far been stated in qualitative terms. It is, however, possible to calculate the coefficient of elasticity. As our materials obey Hooke's law for instantaneous loadings, as a first approximation one may assume that the well-known relation

$$d^2y/dx^2 = -\epsilon(M/I) \tag{3}$$

holds good, where y is the deflection at the bending moment and I the moment of inertia of the cross section of the beam, and ϵ the coefficient of elasticity.

It is easy to derive for continuous loading as due to the weight, the expression for the maximum deflection in the center of the beam

$$y_p = \epsilon(pL^4/8I)[5/48 - \tfrac{1}{2}(a/L)^2] \tag{4}$$

and for a single load in the center

$$y_P = \epsilon(PL^3/48I). \tag{5}$$

From the Eq. (5) there follows

$$dy_P/dP = \epsilon(L^3/48I) \tag{6}$$

or

$$\epsilon = (48I/L^3)(dy_P/dP) \tag{7}$$

dy_P/dP is the slope of the elastic-deflection-line $48I/L^3$ is for all beams equal to $(48b^4/12)/L^3 = 4\times 2.27^4/7.61^3 = 0.00024$ cm. The values for ϵ have been entered in Table II and also the reciprocal of ϵ, which is Young's modulus. The latter has been given in kg/cm² to facilitate comparison with technical literature. The load was measured in grams. To express the coefficient ϵ in absolute units, we have therefore

$$\epsilon = (0.00024/980)(dy_P/dP)$$
$$= 25\cdot 10^{-8}(dy_P/dP)(\text{cm}^2/\text{dyne}). \tag{8}$$

If ϵ is known, Y_p, i.e., the deflection due to the weight of the beam can be computed from Eq. (4), where $a/L = 3.9/76.1 = 0.051$, $p = 10.6\times 980 = 10388$ dyn, $I = (1/12)2.27^4$ cm⁴. These values also have been entered in Table II.

These investigations are being continued with a view of determining numerical values for the yield value, mobility and elasticity in their dependence on the proportion of the solid and liquid phase in the mortar.

We are indebted to Professor W. S. Lohr for advice regarding the construction of the apparatus used and to Mr. W. P. Lewis for assistance in preparing the beams. Mr. Paul A. Balon and Mr. Louis Bertrand assisted in building the apparatus. We are glad to here express our gratitude to those benefactors who have made this research possible.

Appendix I

Calculation of maximum stress in beam under dead load

The density ρ of the cement and mortar stone was found to be fairly equal and on the average $\rho = 2$. The load from the dead weight was therefore $p = 10.6$ g/cm. The bending moment (see Fig. 5) at a distance X from the support is:

$$Mx = (p/2)(Lx - x^2 - a^2) \tag{9}$$

and the maximum bending moment

$$M_{L/2} = (p/2)[(L/2)^2 - a^2] = 9220 \text{ g/cm}. \tag{10}$$

The moment of resistance is $R = b^3/6 = 2.27^3/6 = \smile 2$ cm³. Here b is the thickness of the beam.

As the material obeys Hooke's law, the stress can be calculated as

$$\sigma = M/R = 9220/2 = \smile 4600 \text{ g/cm}^2$$
$$= 45\cdot 10^5 \text{ dyne/cm}^2 = 65 \text{ lbs/in}^2.$$

This is much below the usual working stress in concrete.

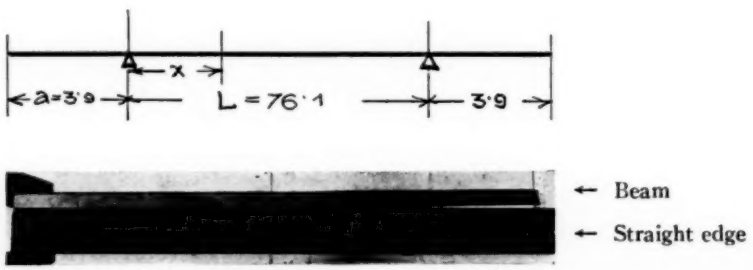

Fig. 5. Beam No. 4 at the age of 165 days.

Kinematic Viscosities and Times of Outflow from Commercial Viscometers

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THE expression of viscosity in terms of the units particular to the various types of commercial viscometers introduces difficulties which would be eliminated by the international acceptance of the c.g.s. units. In certain instances, definite steps have been taken in this direction which include the present policy of the British Air Ministry of quoting viscosity in terms of absolute units (poise). The adoption of the poise as an international unit of viscosity, however, imposes the necessity for the determination of density. The unit of kinematic viscosity (called a stoke by Jakob[1]) which does not involve a knowledge of the density appears to be more acceptable for the purpose in question. It is of interest to note, therefore, that the International Committee on Transformer Oils has expressed itself in favor of denoting viscosity in units of kinematic viscosity.[2]

In view of the wide use of the Engler, Redwood and Saybolt viscometers, any movement directed towards the universal adoption of kinematic units would be assisted by the existence of authoritative tables correlating kinematic viscosity with times of outflow over the whole working range of each commercial viscometer.

The existence of such tables would also afford other advantages:

(1) Independent laboratories could standardize their viscometers as follows: Having determined the kinematic viscosities of a number of oils by a suitable method (e.g., B.E.S.A.,[3] Bingham or Vogel-Ossag viscometers), the standard times of outflow could be obtained from the appropriate standard table or by the use of conversion formulae. Hence, if the observed times of outflow from the instrument did not coincide with the standard times, appropriate corrections could be calculated and made the basis of a correction chart to be used with that particular viscometer. This procedure appears to be preferable to the use of oils of known times of outflow from the national standard viscometer, which has been suggested in the U. S. A. for the calibration of Saybolt Viscometers.[4] While the latter system presents many advantages, it also introduces errors which arise out of the tendency of oils to change their viscosity when stored for a length of time, as is instanced, for example, by the increase of approximately two percent in four years of the Saybolt universal time of oil No. 16515 used by the A.P.I. Committee on Viscosity Standards.

(2) The kinematic viscosities of oils could be converted into times of outflow from any national standard viscometer, and, the two units being interchangeable, this would make it possible to effect a gradual change-over until the petroleum industry as a whole became familiar with the kinematic units. Further, as only small samples of oil are required in the determination of kinematic viscosities, the other advantages afforded by authoritative tables of conversion are obvious.

There is, however, a difficulty confronting the international use of kinematic viscosity units, in that times of outflow are determined at temperatures which vary with the viscometer employed. The temperatures normally used are (1) the Redwood viscometer: 70°F, 140°F, 200°F and occasionally 100°F and 250°F; (2) the Saybolt universal viscometer: 100°F, 130°F and 210°F, and the Furol viscometer: 122°F; (3) the Engler viscometer: 20°C, 25°C, 50°C and 100°C. The interconversion of times of outflow of an oil from different viscometers, therefore, involves the evaluation of viscosities on one viscometer at

[1] Jakob, Zeits. f. tech. Physik 9, 21 (1928).

[2] Olii Minerali e Grassi 9, 18 (1931).

[3] British Engineering Standards Association, Specification No. 188, 1929.

[4] *Report of the Committee on Viscosity Standards, A. P. I.*, p. 6, 1922–24.

temperatures other than those used with that viscometer.

The simplest method appears to be the use of graph papers similar to those devised by Herschel,[5] MacCoull,[6] Sloane and Winning,[7] Larson[8] and Walther.[9] These charts differ in size, method of ruling and system of units. For the sake of accuracy and uniformity, Committee D-2 on Petroleum Products and Lubricants of the American Society of Testing Materials has issued, as a tentative standard, a new viscosity-temperature chart which incorporates the best features of all the previous charts used, particularly the generally-used charts of Larson and MacCoull.[10] By these means, the kinematic viscosities corresponding to the times of outflow at two or more temperatures may be used to determine, by interpolation from a straight-line curve, the viscosity of the oil at the desired temperature. The accuracy of such a procedure appears to be in the order of one percent for temperatures below 212°F in the cases of mineral lubricating oils (excepting oils of high pour-point).

Higgins has advanced equations for the conversion of Redwood No. 1[11] and No. 2[12] times into absolute units, and from time to time since then other values for the constants in each equation have been published. Further, changes have been made in the dimensional specifications of the Redwood viscometers, and it is, therefore, necessary to redetermine the value of the constants of viscometers which conform to the most recent specifications of the Institution of Petroleum Technologists.[13]

The method employed for this purpose entails the determination of the kinematic viscosities and times of outflow of several oils and plotting the quantities ν/T and $1/T^2$ as ordinates and abscissae respectively. From the Higgins diagram so obtained, the values of the constants A and B applicable to the viscometer may be derived. By substitution of these values in the general equation,

$$\nu = AT - B/T. \qquad (1)$$

In the present work the Redwood viscometers, receiving flask and room were at 70°F, so that the values of A and B in this equation may be applied only to Redwood times of outflow determined at room temperatures of approximately 70°F.

According to several workers, the curve mentioned is a straight line, so that one value for each constant has been used for any given value of T within the working range of the commercial viscometer. However, the results obtained from the investigation of the Redwood viscometers lead to curves (see, for example, Fig. 1, curve 3, for the Redwood No. 1 viscometer and Fig. 2, curve 2, for the Redwood No. 2 viscometer, and compare these with Fig. 3, curve 6, for the Saybolt universal and with Fig. 2 curve 5, for the Saybolt Furol) which consist of a straight line for low times of outflow and an inflection which indicates that the values of the constants A and

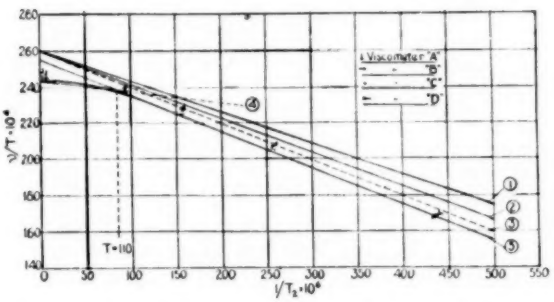

FIG. 1. Higgins diagrams. Redwood No. 1 viscometers. Multiple cup viscometer. Showing results for viscometers A, B, C and D.

Curve 1. Higgins' values, $A=0.00260$, $B=1.715$.
2. Herschel's value, $A=0.00260$, $B=1.88$.
3. Present paper, $A=0.00260$, $B=2.0$, $T''<110$. This curve represents the upper limits of the values of the constants of the viscometers A, B, C and D.
4. Approximation curve, $A=0.002435$, $B=0.6$ (viscometer D) $T''>110$.
5. Present paper, $A=0.00255$, $B=2.0$ (viscometer D) $T''<110$. This curve represents the lower limits of the values of the constants of viscometers A, B, C and D.

Curves 3 and 5 represent minimum and maximum values of the constants A and B for Redwood No. 1. Viscometers A, B, C and D. $T''<110$.

[5] Herschel, Ind. Eng. Chem. **14**, 715 (1922).

[6] MacCoull, Lubrication, No. 7, Part 6, p. 5; International Critical Tables **2**, 147 (1926).

[7] Sloane and Winning, Ind. Eng. Chem. **23**, 673 (1931).

[8] Larson, J. S. A. E. **28**, 325, 487 (1931).

[9] Walther, Erdol und Teer **5**, 619 (1929); Petroleum Zeits. **26**, 755, 822 (1930).

[10] A. S. T. M. Bulletin, p. 5, March, 1932.

[11] Higgins, Collected Researches of the N. P. L. **9**, 1 (1914).

[12] Pannel and Higgins, ibid. **13**, 265 (1916).

[13] *Standard Methods of Testing Petroleum and Its Products*, I. P. T. London, 1929.

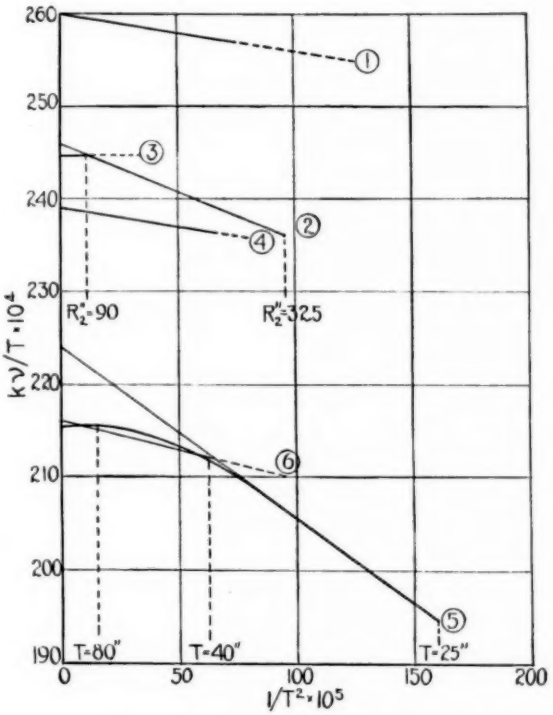

FIG. 2. Higgins' diagrams. Redwood No. 2 and Saybolt Furol viscometers.

Curve 1. Barr's tentative values, $A=0.026$, $B=0.40$.
2. Present paper, $A=0.02458$, $B=1.0$, $T''>90$.
3. Present paper, approximation curve, $A=0.02447$, $B=0$, $T''>90$.
4. Herschel's values, $A=0.0239$, $B=0.403$.
5. Curve to A.P.I. data for Saybolt Furol. Present paper, $A=0.0224$, $B=1.84$, $T''>25$ to 40.
6. Saybolt Furol approximation curve. Present paper, $A=0.0216$, $B=0.6$, $T''>40$.

B gradually diminish from a given value of time of outflow T_1 until another higher value T_2 is reached. For values of T greater than T_2, the value of the constant B becomes zero,[14] so that the general Eq. (1) is reduced to the simpler form:—$\nu=A_1T$, where T is greater than a certain number T_2.

The variation in the values of the constants A and B with times of outflow had already been noted by the A.P.I. Committee on Viscosity Standards (1922 to 1924)[4] in its examination of the Saybolt viscometers, and one set of values for these constants was published for application to a limited range of low times of outflow. Provision was also made for the conversion of a higher range of times of outflow by substituting another value for the constant A in an equation of the form: $\nu=AT$, that is to say, the constant B is zero for this range. The report mentioned, however, did not provide a conversion equation for an intermediate range of Saybolt times. Consequently, the method of approximation employed in the case of the Redwood viscometer has been applied to the data in the report, resulting in a second conversion equation which may be applied to these intermediate and the higher values of Saybolt seconds. Two equations are thus obtained which cover the whole working range of the Saybolt viscometers.

The Engler viscometer, on the other hand, has also been examined by several workers who have published widely different values of the constants and also equations of different forms. The conversion equation at present accepted in Germany is complicated, as apparently an attempt has been made to devise one equation for the conversion of all times of outflow down to that of water at 20°C. The validity of the

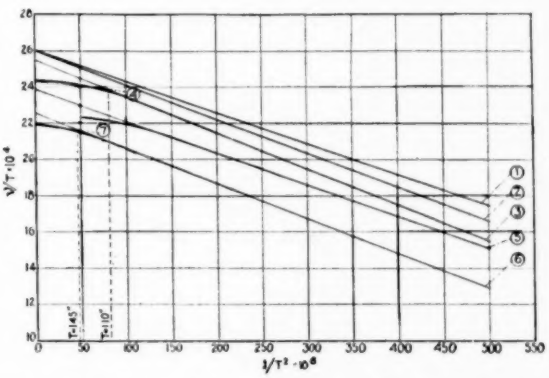

FIG. 3. Higgins' diagrams. Redwood No. 1 and Saybolt universal viscometers.

Curve 1. Higgins' values, $A=0.0026$, $B=1.715$.
2. Herschel's values, $A=0.0026$, $B=1.88$.
3. Present paper, $A=0.00255$, $B=2.0$ ($T''<110$) viscometer D.
4. Approximation curve, present paper, $A=0.002435$, $B=0.6$ ($T''>110$) viscometer D.
5. Present paper. Data of Savill and Cox. (Temp. 70°C–100°C).
6. Curve to A.P.I. data for Saybolt universal, $A=0.00226$, $B=1.95$ ($T''>32$ to 145).
7. Saybolt universal approximation curve, $A=0.00220$, $B=0.8$ ($T''>145''$).

[14] The unexpected inflection in the curve was found to be characteristic of several Redwood No. 1 viscometers, and in order to obtain an equation of the general form which could be applied to values of T greater than T_1 (approximately) a method of approximation was employed to derive a second set of values for the constants A and B which is given later under the description of the Higgins diagram.

equation has recently been confirmed by Erk,[15] but we have been unable to trace the publication of his experimental data. The only matter available was a table of kinematic viscosities and Engler degrees which were calculated by means of the cubic equation originally advanced by Vogel[16] for the Engler viscometer.

The figures have been utilized to draw a Higgins diagram which is a sigma-type of curve (Fig. 4). An examination of this shows that if one

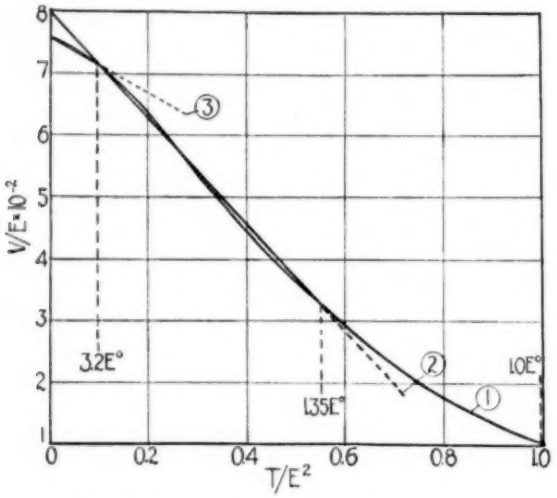

FIG. 4. Higgins' diagram. Engler viscometer based on Vogel's equation and Erk's tables.
Curve 1. Vogel's equation $v = E/100 \times 7.6^{(1-1/E^3)}$ and Erk's tables.
2. Approximation curve, $A = 0.08$, $B = 0.0864$, $E°$ from 1.35 to 3.2°.
3. Approximation curve, $A = 0.076$, $B = 0.04$, $E°$ above 3.2°.

ignores the lower right-hand inflection, which discloses the turbulent nature of the flow for the lowest range of Engler degrees, the rest of the curve is found to possess the general characteristics already found to exist in those for the Redwood and Saybolt viscometers, namely, certain values for the constants A and B are valid for a small range of the lower rates of flow, above which the value of the constant B steadily diminishes to zero. The method of approximation, above outlined, has, therefore, been applied to Erk's Engler degrees—Kinematic Viscosity Table,[15] to give two sets of values for the constants A and B by means of which Engler degrees, excepting a very small range of the lowest values, may be converted into kinematic viscosities.

The above conclusions were reached early in 1931 since when the second report of the A.P.I. Committee on Viscosity Standards (1931) has appeared. While this report confirms the data given in the first report showing the relationship between Saybolt times and kinematic viscosities, some of the data contained in it indicate a further difficulty which apparently confronts the movement directed towards the universal adoption of kinematic units for the expression of viscosity in commerce. Particular reference is made to the kinematic viscosities of the Alpha oil determined with a Vogel-Ossag viscometer at various temperatures.[17]

The kinematic viscosity of a sample of Alpha oil was determined by means of N.P.L. certified U-tube viscometers of the type recommended by the B.E.S.A.,[3] the Institution of Petroleum Technologists[13] and other bodies. The temperature control at 70°F was of the order of ±0.02°F (corr.), and the kinematic viscosity of the Alpha oil at this temperature was approximately 1.8 percent lower than the corresponding figure quoted in the 1931 report. This lower figure agreed closely with that obtained in a similar way six months earlier on a different sample of Alpha oil.

As a check on the uniformity of these two samples of Alpha oil, the corrected Redwood No. 1 times of outflow were determined at 70°F, and the two figures so obtained agreed very closely with the corrected Redwood No. 1 times at 70°F given in the 1931 report for laboratories A and B.[18]

These differences between kinematic viscosities determined on the same oil by different methods naturally would affect the values of A and B thus: Take the average Redwood No. 1 times determined by laboratories A and B for the Alpha oil at 70°F as 712 seconds. If one accepts the (Vogel-Ossag) kinematic viscosity of the Alpha oil at this temperature to be 1.799, then the value for the constant A in the equation

[15] Erk, Zeits. f. tech. Physik **8**, 595 (1927); Z. Ver. deut.-Ing. **72**, 11 (1928); Forschungsarbeiten, V. D. 1, Heft 283 (1928); Petroleum **24**, 830 (1928).

[16] Vogel, Zeits. f. angew. Chemie **35**, 561 (1922).

[17] *Report of the Committee on Viscosity Standards, Div. of Refining*, p. 15, 1931.

[18] Reference 17, p. 12.

$\nu = AT$ (which is valid for a time of outflow of 712 seconds) is 0.002527 which is at variance with the value of 0.00247 found by work involving the B.E.S.A. U-tube method for kinematic viscosity.

Similar conclusions have been drawn from a comparison of the most accurate figures available to the authors for the conversion of Saybolt times to Redwood times. These conclusions confirm the suggestion that a difference exists between the kinematic viscosity quantities used to convert Saybolt times, on the one hand, and Redwood times, on the other, into kinematic units.

These discrepancies which appear to exist between the kinematic viscosities of an oil determined by different absolute viscometry methods may be due to the differences between either the construction and manipulation of the viscometers or the method employed by different bodies for the calibration of the absolute viscometers or to errors in thermometry.

The variations observed form another obstacle confronting the use of kinematic viscosity units, and it can only be removed by international cooperation designed to unify the methods of determining the viscosities in absolute units or to demonstrate the degree of agreement attainable by the use of either similar or different methods in laboratories situated in different countries.

These observations point to the conclusions that: (1) Until the desired conformity among absolute viscometry methods is demonstrated or realized, the international use of kinematic viscosity units may not be accepted as a basis for the correlation of the readings given by the principal national commercial viscometers; (2) in the circumstances, the best available method for this purpose is a *direct* comparison of the various national standard viscometers, the Engler, Redwood and Saybolt.

Fig. 5 is a chart showing the interrelationship of various types of commercial viscometer based on the equations given later in the report. This means of interconversion is approximate only and is valid only, if the viscometers giving the readings to be converted have been standardized or calibrated against a standard viscometer (Redwood and Saybolt), or in the case of the Engler instrument if it agrees with the Engler viscometer on which Vogel's equation is based.

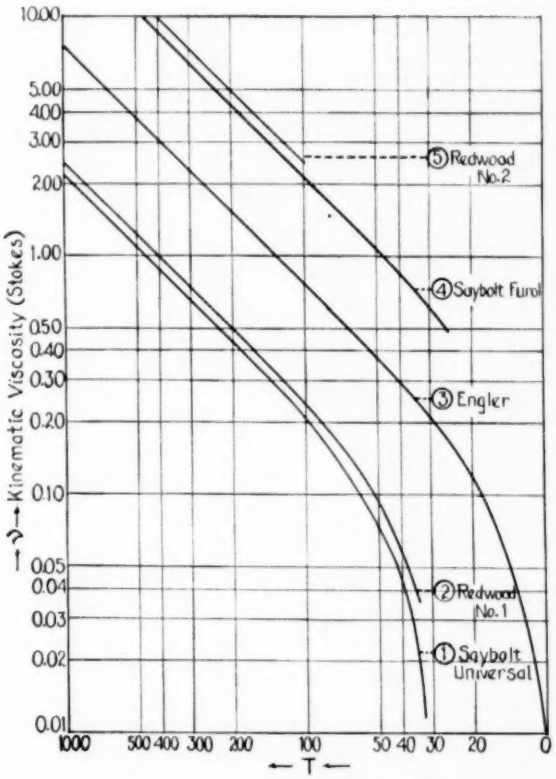

FIG. 5. Chart for interconversion of commercial viscometer readings and kinematic viscosity. For curves 1, 2, 4 and 5, T = seconds; for curve 3, T = degrees × 10.

Curve 1. The Saybolt universal viscometer based on equations given on pp. 109, 110.
2. The Redwood No. 1 viscometer based on equations given on p. 107.
3. The Engler viscometer based on Vogel's equation given on p. 111.
4. The Saybolt Furol viscometer based on equations given on pp. 109, 110.
5. The Redwood No. 2 viscometer based on equations given on p. 109.

Factors for high values of ν outside the range of this chart and/or above $\nu = 2.5$ stokes:

$\nu =$	$R_1'' =$	$R_2'' =$
$0.00247 \times R_1''$	$405 \times \nu$	$40.5 \times \nu$
$0.00220 \times S_u''$	$0.89 \times S_u''$	$0.1 \times R_1''$
$0.02470 \times R_2''$	$10 \times R_2''$	$0.089 \times S_u''$
$0.02160 \times S_F''$	$8.74 \times S_F''$	$0.874 \times S_F''$
$0.0760 \times E°$	$30.8 \times E°$	$3.08 \times E°$

$S_u'' =$	$S_F'' =$	$E° =$
$455.5 \times \nu$	$46.3 \times \nu$	$13.16 \times \nu$
$1.123 \times R_1''$	$0.1135 \times R_1''$	$0.0324 \times R_1''$
$11.23 \times R_2''$	$0.102 \times S_u''$	$0.0290 \times S_u''$
$9.82 \times S_F''$	$1.135 \times R_2''$	$0.324 \times R_2''$
$34.55 \times E°$	$3.52 \times E°$	$0.284 \times S_F''$

The effect of temperature on the conversion of the readings obtained by the commercial viscometers is discussed later in the present paper.

The Higgins Graphical Method for Evaluating the Constants A and B

The experimental data required are a number of kinematic viscosities (ν) and times of outflow of several oils, each pair of determinations being carried out at the same temperature. The quantities ν/T and $1/T^2$ are then plotted on a large scale as ordinates and abscissae, respectively.

It will be appreciated that, if the general equation: $\nu = AT - B/T$, that is, $\nu/T = A - B/T^2$ applies over the whole range of the commercial viscometer, the line representing the relationship will be straight; the value of the constant A will be indicated by the point of intersection of the straight line (or its projection in some cases) and the Y axis, the slope of the curve giving the value of the constant B (see Fig. 1).

In addition, Higgins diagrams obtained in certain cases will indicate the time of outflow where there is an alteration in the nature of the flow of the oil through the viscometer capillary, that is, it will indicate the lower limit of the useful range of the viscometer. The commencement of the change-over from streamline to turbulent flow is indicated by a change of slope (a decrease) which takes place when times of outflow are small, in which cases the rate of flow through the capillary is very high.[19]

This method has been used by many experimenters and has been applied in the present paper to experimental results obtained with a Redwood No. 1 viscometer and No. 2 viscometer (see below). It was found necessary, however, to take the preliminary precaution of plotting the experimentally-determined values of kinematic viscosities against times of outflow on a large scale to give a smooth curve which levels out small errors of timing which are incurred more especially with oils having small times of outflow (60 to 40 seconds). This curve is then used to give corresponding values of ν and T from which the quantities ν/T and $1/T^2$ are calculated for the above-mentioned purpose. Otherwise, small timing errors markedly affect the corresponding values of $1/T^2$ and make it less easy to draw the curve from which the values of the constants A and B are derived.

[19] Herschel, Bur. Stand. Tech. Paper, No. 210, p. 240, Fig. 6, 1922.

The Standardization of Commercial Viscometers

In the standardization of commercial viscometers, it is usual to determine the time of outflow of water or oil under standard conditions of test, in addition to the check on the various dimensions of the viscometers.

The procedures employed for this purpose in America, England and Germany are different in several important details. The Saybolt viscometers, for instance, are compared against the master tube at the Bureau of Standards by a comparative flow test with *one* oil. (The oil used for the Saybolt universal has a time of outflow of approximately 200 seconds at 100°F.) The Engler viscometers are standardized by observing the water rate at 20°C, which is divided into all observed Engler seconds to give the Engler degrees or relative viscosity of the oil. The water rate should be between 50 to 52 seconds as a further check on the dimensions of the instrument.

At one time, the National Physical Laboratory, England, adopted the procedure for Redwood viscometers, involving one comparative flow-test at *room* temperature with an oil having a Redwood time of outflow of approximately 300 to 400 seconds. However, since the issue of the 1929 specification of the Institution of Petroleum Technologists,[13] the standardization has consisted of two comparative flow-tests with oils having Redwood No. 1 times 300 to 400 seconds and 60 to 70 seconds, respectively, at room temperature.

The corrections for times of outflow above 400 seconds and between 400 and 70 seconds are then obtained by a graphical method in which the Higgins diagram for the standard instrument is used to calibrate that obtained for the viscometer under test on the basis of the comparative flow times.[20] A similar list of corrections is used in our laboratory for constructing a correction chart from which the corrections in seconds corresponding to any observed reading may be obtained.

The necessity of two comparative flow-tests appears to have been realized by the responsible authorities in Britain because standard Redwood

[20] Barr, J. Sci. Inst. 7, 359 (1930).

No. 1 viscometer No. 1307 does not satisfy the dimensional specification[21] which was framed in 1929 in order to provide greater uniformity between Redwood No. 1 viscometers. Evidence in support of the necessity for comparative flow-tests with two oils of *widely* different times of outflow is to be found in the words of the late Sir Boverton Redwood:[22] "In the original standardizing of the instrument, slight departures from the standard size of orifice may be corrected by placing the gauge point a little higher or lower. If, however, there be any considerable deviation from the model, especially in respect to height of column of oil, the instrument may be standardized to give the same results as the pattern with *a certain oil* but will not necessarily furnish concordant results with another oil of different viscosity."

An example of the magnitude of the variations of the corrections for different times of outflow which can result from deviations in dimensions is given by Barr[20] who says that while an instrument (conforming to the I.P.T. specification, 1929) may require a correction of −1.5 percent at times of outflow of 350 seconds, a correction of −4.0 percent may be required at 65 seconds.

At first sight, therefore, two comparative flow-tests may appear unnecessary for the Engler and Saybolt viscometers, since better uniformity of dimensions may be expected between viscometers of the same type in which all the parts of these viscometers are metal, whereas the jets of the Redwood viscometers, being agate, are not so easily machined. The evidence available, however, supports the belief that the standardization of the Engler viscometers by checking the dimensions and limiting the water rate at 20°C to from 50 to 52 seconds is quite inadequate.

In the first place, one has the statement by Herschel[23] that water is an undesirable liquid with which to standardize the Engler viscometer, since turbulent flow is established at approximately 1.1°E. Barr[24] also supports the view that the condition of turbulent flow is unsuitable for the determination of viscosity. In the second place, one has the experimental results of Weick[25] who examined two Engler viscometers with dimensions which satisfied the Engler specification. The water rates of both viscometers were within the limits and differed by only 0.4 second (i.e., approximately 0.8 percent). Three oils examined on each viscometer, however, gave pairs of Engler degrees which varied by from 3.65 percent to 4.8 percent.

It would not be surprising, therefore, if several Saybolt viscometers of recent construction, which agree at times of outflow of approximately 295 seconds for the Universal at 100°F and of 116 seconds for the Saybolt Furol at 122°F, disagreed chiefly with oils of small times of outflow.

It is felt, therefore, that the practice of standardization of commercial viscometers with two oils with times of outflow wide apart, as is adopted by the National Physical Laboratory for the Redwood viscometers, probably would be equally desirable also for the Saybolt viscometers. As there is no national standard Engler instrument, this method cannot be employed at present. An alternative and probably more desirable method is definitely to base the calibration of Engler viscometers on kinematic viscosity by the use of the Vogel equation and Table XII given by Erk (reproduced at the end of the paper).

Effect of Temperature of Test on the Values of Constants *A* and *B*

No experimental work on the effect of temperature on the constants is recorded in this paper, but some light is thrown on this subject by previous workers.

Waidner,[26] who derived conversion tables for the Saybolt universal, Engler and Redwood viscometers in 1915, stated that the Saybolt-Engler factors varied only with the viscosity of the oil. The Saybolt-Redwood factors, on the other hand, varied with the viscosity *and with the temperature.* In the latter case, the conversion factors were greater when the efflux times were obtained at low temperatures than when the

[21] Barr, *Monograph of Viscometry*, p. 93, 1931.

[22] Redwood, *Treatise on Petroleum*, p. 602, 1906 Edition; p. 825, 1926 Edition.

[23] Herschel, Bur. Stand. Tech. Paper, No. 100, 1917; Proc. A. S. T. M. **17** (ii), 551 (1917).

[24] Barr, *Monograph of Viscometry* p. 42, 1931.

[25] Weick, Congrés du Graissage, Strasbourg, 1931.

[26] Waidner, Proc. A. S. T. M. **15** (i), 284 (1915).

same efflux times were found with other oils at higher temperatures.

This anomaly can probably be explained by the difference in the operation of the various instruments, taken in conjunction with the fact that the jet in the Saybolt and Engler instruments is not exposed to contact with air which causes anomalous cooling to take place with the Redwood viscometer. This variation is probably accentuated also by the use of an agate jet in the Redwood instrument as compared with a metal jet in the Saybolt and Engler apparatus.

An examination of the effects of temperature was made by drawing curve 5, Fig. 3, with the aid of the published data of Savill and Cox[27] on absolute viscosities, densities and Redwood times for oils at 70°C and 100°C. This curve is similar in shape to curve 3 (described later for our Redwood No. 1 viscometer at 70°F), but it approaches the horizontal at $\nu/T = 0.002235$, and, although the curve is incomplete, the indications are that it would steadily drop to a point where ν/T is approximately 0.00220 for a Redwood time of 280 seconds. This last feature is probably mainly due to the cooling of the oil during the determinations causing higher observed readings than the true efflux time, since Herschel[19] has stated that there is no change in the instrumental constants due to variation in the temperature of the test.

One consideration resulting from this is that efflux times at high temperatures should be corrected for cooling error, and this may be done in a manner suggested by Herschel.[19]

Another conclusion to which we are driven is that a careful reinvestigation of the effects of the temperature of test on the constants is still required in view of the results of Waidner, Savill and Cox, and the more recent work of Herschel.[28] The latter aspect of the problem will probably be affected by the anomalous behavior of the principal commercial viscometers at high temperatures (200 to 210°F approximately) when water or oil is used as the heating medium in the viscometer bath. It is well known that when oil is used as the heating medium in the viscometer bath a higher bath temperature is required to maintain thermal equilibrium of the oil in the viscometer cup than when water is employed. However, our experiences with the Redwood viscometer show that, when water is used in the outside bath at 200°F, the times of outflow are *smaller* than when oil is used as the bath liquid, even though the bath temperature required with water is lower than that with oil; and in each case the thermometer in the oil cup registers 200°F (corr.) throughout the run, without appreciable variation.

This anomaly does not appear to have been commented on by previous workers (which is not surprising in view of the lack of standardization on the question of bath liquids), and thus variations of the constants with temperature may have been masked during previous investigations.

With the Engler and Saybolt viscometers, an opposite effect may be experienced, since in both these viscometers the metallic jets are in closer contact with the heating medium than the agate jet of the Redwood No. 1 viscometer which is in contact all over its outside surface with the metal base of the oil cup. So far as the Saybolt viscometers are concerned, some concern is expressed in the second A.P.I. report about the effect of the higher temperature employed at 210°F with oil in the Saybolt universal bath and its probable effect of giving lower times of outflow.[29]

Mr. Herschel informs us, however, that, if the A.S.T.M. standard method is strictly followed as regards equilibrium temperature of bath, a steam-heated water bath and an electrically-heated oil bath will give the same times of outflow on the one oil, although the oil-bath temperature is higher.

The Redwood No. 1 Viscometer

The generally accepted values of A and B (0.00260 and 1.715, respectively) for this viscometer were determined by Higgins on the standard Redwood No. 1 viscometer No. 1307 (curve 1, Fig. 1), but they have been criticized by both Herschel[19] and Barr.[30] The former concluded from his own experiments that Higgins' value for A was probably correct but that the value for B should be 1.88 (curve 2, Fig. 1), and the latter

[27] Savill and Cox, J. S. C. I. **35**, 351 (1916).

[28] Herschel, J. I. E. C. **15**, 945 (1923).

[29] Reference 4, Division of Refining, p. 9, 1931.

[30] Barr, Aero. Research Committee, R. and M., No. 906, 1923; *Monograph of Viscometry*, p. 92, 1931.

TABLE I. *Redwood No. 1 viscometer.*

A	*B*	Reference
Values of A and B from results of previous workers		
0.00260	1.715	Higgins, Petroleum World. (June and July, 1913); Coll. Researches N.P.L. **9**, 1 (1914); J.S.C.I. **32**, 568 (1913); Redwood viscometer No. 1307. Redwood times on 8 oils at different temperatures (10°C to 60°C).
0.002322	1.387	Upton, Proc. A.S.T.M. **15** (i) 297 (1916); Redwood viscometer 1004.1205. Upton applied Higgins graphical method to data of Waidner, ibid, 284.
0.002631	1.577	Flowers, ibid, 318. Calculated from data of Meissner Chem. Rev. Fett-Harz. Ind. **19**, 30 (1912).
0.00260	1.561	Herschel, Proc. A.S.T.M. **17**, 552 (1917). Calculated from Meissner's equation (loc. cit.).
0.00260	1.88	Herschel, Bur. Stand. Tech. Paper No. 210 (1922).
0.00240	0	Anon, Electricity **33**, 237 (1919). Suggested with reservations for calculating kinematic viscosities of oils from Redwood times of outflow 185 to 3700 seconds approximately.
0.00223	1.47	International Electrotechnical Commission. Advisory Committee on Insulating Oils. **10** Gt. Britain (32) 6 (September, 1927).
0.0026	1.7	I.P.T. Standard Methods of Testing 66 (1929).
0.00255	1.715	Barr, Aero Research Comm. R. & M. No. 906 (1923). Deduced from Higgins' data (loc. cit.) having assumed $B=1.715$ (±10 percent).
Results given in present paper		
0.00238	1.75	For Redwood times up to 100 seconds approximately Higgins' graphical method applied to data of Savill and Cox, J.S.C.I. **35**, 151 (1916), for oils tested at 70°C and 100°C in a Redwood viscometer (no cooling corrections applied).
0.00250	1.65	For Redwood times up to 98 seconds.
0.00238	0.48	For Redwood times between 98 and 100 seconds. Deduced by applying Higgins' graphical method to data published by Archbutt and Deeley, *Lubrication and Lubricants*. 226 (Table LXVIII) (1927), for glycerol-water mixtures. See also value of *k*, 234 (Table LXXI), for high values of Redwood seconds at room temperature.
0.00255	2.0	For Redwood times from 34 approximately to 110 seconds. Our viscometer.
0.002435	0.6	For Redwood times over 110 seconds. Our viscometer.
0.00260	1.79	For corrected or standard Redwood No. 1 seconds 34 to 100 seconds.
0.00247	0.5	For corrected or standard Redwood No. 1 seconds 100 to 1000 seconds.

concluded from a survey of Higgins' experimental data that the value of A should be 0.00255.

An examination of the literature disclosed the disparity between the results of numerous workers in this field, and these results are summarized in Table I. A most interesting contribution is that of an anonymous writer who suggested, with reservations, in 1919 that the equation: $\eta = ATd$, i.e., $\nu = AT$ could be used for oils with absolute viscosities between 0.4 and 8.0 poises (approximately 185 to 3700 Redwood seconds), and he advanced a value of 0.00240 for the constant A in his equation. A similar value (0.00239) for the constant applicable to Redwood times of 175 to 2930 seconds can also be deducted from the data to be found in the early editions of *Lubricants and Lubrication* by Archbutt and Deeley (see Table I). These results are important since they corroborate our experimental results which were obtained before a close scrutiny of the literature had been made.

A Redwood No. 1 viscometer found to satisfy the 1929 specification of the I.P.T. was used for our work. A series of 16 mineral oils having Redwood No. 1 times of outflow between 44 and 2286 seconds were taken, and during selected periods when the laboratory was between 69°F and 71°F their times of outflow were determined at 70°F. The thermometers and the 50 ml viscometer flask had been calibrated previously by the National Physical Laboratory.

The kinematic viscosities were determined at 70°F with U-tube capillary viscometers described in the specification No. 188 (1923) of the British Engineering Standards Association and accepted by the I.P.T. in 1929. The constants of these instruments had been determined by the N.P.L. and certified to be correct to within ±0.25 percent, and the water thermostat employed was maintained at 70°F±0.02°F (corr.).

The experimental data so obtained (Tables II and III) were employed in the manner previously described to give a Higgins diagram for the viscometer (curve 3, Fig. 3) which has the in-

TABLE II. *Redwood No. 1 viscometer, temperature at 70°F (corr.).*

Oil No.	Observed Redwood No. 1 (seconds)	Kinematic Viscosity		
		Observed	Calculated*	Percent difference
1	43.9	0.0671	0.0664	−1.2
2	47.2	0.0775	0.0780	+0.7
3	54.0	0.1001	0.1007	+0.5
4	61.1	0.1232	0.1231	−0.1
5	75.0	0.1660	0.1645	−0.7
6	81.7	0.1850	0.1838	−0.53
7	95.0	0.2210	0.2210	0.0
8	117.4	0.2804	0.2810	+0.15
9	173.6	0.4180	0.4190	+0.23
10	215.5	0.5220	0.5220	0.0
11	294.0	0.7160	0.7190	+0.35
12	395.5	0.9610	0.9610	0.0
13	560.5	1.3650	1.3640	−0.07
14	721.6	1.7570	1.7560	−0.07
15	1235.0	3.0110	3.0060	−0.01
16	2286.0	5.5170	5.5920	+1.4

* Calculated by formulae derived for the viscometer.

TABLE III. *Redwood No. 1 viscometer, temperature 70°F (corr.).*

Taken from Smooth Curve Redwood No. 1 (seconds)	Kinematic viscosity	Calculated kinematic viscosity†
45	0.0705	0.0703
50	0.0875	0.0874
55	0.1040	0.1040
60	0.1200	0.1200
65	0.1350	0.1350
70	0.1500	0.1500
75	0.1650	0.1650
80	0.1790	0.1790
85	0.1930	0.1930
90	0.2075	0.2070
95	0.2210	0.2210
100	0.2345	0.2350
105	0.2480	0.249
110	0.2610	0.2620
120	0.2860	0.287
130	0.3120	0.3120
140	0.3370	0.337
150	0.3615	0.361
160	0.3870	0.386
170	0.4115	0.410
180	0.4355	0.435
200	0.4855	0.484
220	0.5340	0.533
260	0.6320	0.631
300	0.7300	0.729
330	0.8035	0.802
360	0.876	0.875
400	0.974	0.973

† Calculated by formulae derived for the viscometer.

flection already mentioned. That this inflection was a fundamental characteristic of the Redwood No. 1 viscometers generally, was shown as follows: Four Redwood No. 1 viscometer cups were assembled in a multiple viscometer bath into the top of which water was fed at a constant temperature of 70°F. The water was withdrawn from the bottom of the bath through a constant level device fixed diametrically opposite to the point of entry, and, in addition, a circulatory motion was imparted to the water by a central belt-driven propellor shaft. The surrounding-air temperature was 70°F, and thus all the cups were easily maintained at the uniform temperature of 70°F. The times of outflow from each of the cups were determined for a new series of six oils having Redwood No. 1 times 570, 396, 104, 80, 63 and 48 seconds approximately. Having already measured the kinematic viscosities, the values of ν/T and $1/T^2$ for each oil cup were plotted *directly* on to the Higgins diagram (curve 3, Fig. 3, reproduced in Fig. 1). The curves for these viscometers are similar in shape, although the constants A and B for each viscometer are slightly different.

It will be noticed that curve 3, Fig. 3, is made up of three parts: (1) a short length on the left which is practically horizontal for which $A=0.002435$ and $B=0$ (this observation confirms the statement made in 1919 by an anonymous writer mentioned above); (2) an intermediate curved portion for which a less simple relationship exists between ν and T; (3) another straight limb on the right for which $A=0.00255$ and $B=2.0$.

The possibility of having to use three conversion formulae was removed by drawing a straight line curve 4, Fig. 3, which averages the points on the upper part of curve 3. The values of A and B for this approximation line are $A=0.002435$ and $B=0.6$.[31] Hence two formulae were derived:

(1) $\nu=0.00255\times T-2.0/T$, where $T=34$ to 110 Redwood No. 1 seconds

(2) $\nu=0.002435\times T-0.6/T$, where $T=$ Redwood No. 1 seconds above 110.

[31] While this approximation represents the experimental results within the normal limits of accuracy, it should be noted that it is possible mathematically to obtain a closer approximation to the experimental results by the use of a more complicated equation applicable to all values of T greater than 100 seconds approximately. This was evident when the "kinematic viscosity-Saybolt universal seconds" data published by the A.P.I. Committee were used to give a

The validity of these two formulae was tested by calculating kinematic viscosities corresponding to the observed times of outflow for the sixteen oils used in the first experiments. These calculated values are listed beside the experimentally-determined values in Tables II and III. The percentage differences in the last column show that these equations hold extremely well for the *particular* Redwood No. 1 viscometer used. In order to arrive at a more generally applicable set of equations, the same viscometer has recently been calibrated by comparative flow tests at 400 seconds and 70 seconds (70°F) against Redwood No. 1 viscometer calibrated at the N.P.L. by similar comparative flow-tests with the standard viscometer No. 1307. The correction chart so obtained for the viscometer concerned was used to correct the observed readings to corrected or standard Redwood No. 1 times of outflow. These values together with the previously observed kinematic viscosities were used to draw a Higgins diagram which should closely represent the characteristics of the standard Redwood No. 1 viscometer No. 1307. The equations which were derived from this curve are: $\nu = 0.00260 \times T - 1.79$ (for values of Redwood No. 1 sec. 0.34–100) $\nu = 0.00247 \times T - 0.5/T$ (for values of Redwood No. 1 sec. over 100).

As a recheck on this work, a few determinations of corrected Redwood No. 1 times of outflow have been made with the N.P.L. calibrated viscometer. The kinematic viscosities calculated by means of these equations have been found to agree very closely with the kinematic viscosities determined by the B.E.S.A. U-tube viscometers (at 70°F).

These equations may, therefore, be used to convert corrected Redwood No. 1 times of outflow into kinematic viscosities in place of the Higgins equation which is used at present in many laboratories to convert Redwood times of outflow from 34 to 2000 seconds into kinematic viscosity.

These new equations, however, are only put forward tentatively as it is felt that the equations finally adopted for the Redwood viscometers should be based on actual determinations of times of outflow on a standard viscometer at the National Physical Laboratory.

The Redwood No. 2 Viscometer (Admiralty Type)

The first published values for the constants A and B for this viscometer were given by Pannell and Higgins[12] as 0.027 and 12.0, respectively, but Herschel[32] who examined two viscometers of this type suggested that the quantities 0.024 and 0.403, respectively, were probably more correct. Recently, however, Barr[33] agrees with Herschel that the value of B is about 0.4, but he tentatively suggests 0.026 for the value of constant A (Table IV).

Table IV. *Redwood No. 2 viscometer.*

A	B	Reference
0.0270	12.0	Pannell and Higgins, Coll. Researches N.P.L. **13**, 265 (1916).
0.0270	20.0	Private communication to McKinney Mfg. Co. from N.P.L. Used in *Friction Pressure Losses in Pipe Lines* (1920).
0.0230	0.36	Used by Danforth in *Oil-Flow in Pipe Lines* (1921).
0.0239	0.403	Derived for two Redwood No. 2 instruments by Herschel, Chem. Met. Eng. **26**, 1175 (1922).
0.0260	0.40	Tentative suggestions by Barr, *Monograph of Viscometry*, p. 96 (1931).
Results given in present paper		
0.02458	1.0	For Redwood No. 2 times 32.5 to 90 seconds.
0.02447	0	For Redwood No. 2 times 90 to 650 seconds.
0.0247	0	For corrected Redwood No. 2 times over 100 seconds.

Higgins diagram. In this case an equation of an arc of a circle was found to fit in extremely well, the center of the circle being on the Y axis. When this equation was reduced to a form convenient for calculating kinematic viscosities from Saybolt universal seconds, one got the equation: $\nu = T(0.002034 + 2 \times 10^{-5} \times (64.8025)^{\frac{1}{2}} - X^2)$ where $X = 1/T^2$ and T = Saybolt seconds above 135.

Values of ν calculated by means of this equation and 4-figure tables of the squares and reciprocals of numbers for given values of T were identical with the corresponding values of ν given in the A.P.I. table.

The possibility of representing the changes in the values of the constants A and B, as the efflux time gets greater, by the arc of a circle the center of which lies on the Y axis, provides for a steady decrease in the value of the kinetic-energy constant B to zero at infinitely small rates of flow through the viscometer capillaries. This appears to fall in line with the findings of Dorsey, Phys. Rev. **28**, 833 (1926).

[32] Herschel, Chem. Met. Eng. **26**, 1175 (1922).

[33] Barr, *Monograph of Viscometry*, p. 96 (1931).

A Redwood No. 2 viscometer of recent manufacture has been examined in the manner adopted for the No. 1 viscometer, and special attention was paid to the lower range of times of outflow. Seventeen oils having Redwood No. 2 times ranging from 18 to 650 seconds (approximately 180 to 6500 Redwood No. 1 seconds) were chosen for the work. The observed Redwood No. 2 times of outflow and kinematic viscosities (Table V) were plotted on an open scale, but it was not possible to draw a smooth curve through all the points. The data on the six oils of the lower viscosity range were eventually ignored because a smooth curve could only be drawn through the other eleven points. Probably the onset of turbulence at Redwood No. 2 times about 32 seconds had rendered the first six results of doubtful value.

The kinematic viscosities and corresponding Redwood No. 2 times, used to arrive at curve No. 2, Fig. 2, were read from this curve (Table VI). The Higgins diagram resulting, has an inflection similar to that for the Redwood No. 1 viscometer, curve 3, Fig. 3, but the change of direction takes place so rapidly that an approximation curve of the type drawn for the No. 1 viscometer was unnecessary. The following equations were derived for this particular Redwood No. 2 viscometer: $\nu = 0.02458 \times T - 1.0/T$ for values of R_2 seconds from 32.5 to 90; $\nu = 0.02447 \times T$ for values of R_2 seconds from 90 to 650.

TABLE V. *Redwood No. 2 viscometer, temperature 70°C (corr.).*

Oil No.	Observed Redwood No. 2 (seconds)	Kinematic Viscosity Observed	Calculated*	Percent difference
23	18.2	0.421	——	——
24	20.85	0.492	——	——
25	22.33	0.526	——	——
26	24.05	0.566	——	——
27	26.25	0.633	——	——
28	29.9	0.716	——	——
29	32.35	0.769	.757	−1.5
30	35.5	0.841	.844	+0.34
31	40.0	0.965	.960	−0.53
32	44.8	1.070	1.078	+0.76
33	56.0	1.360	1.359	−0.07
34	69.75	1.698	1.700	+0.10
35	96.85	2.353	2.370	+0.72
36	122.2	2.991	2.990	−0.03
37	210.7	5.152	5.155	+0.06
38	227.8	5.575	5.573	−0.05
39	640.0	15.528	15.661	+0.90

* Calculated by formulae derived for the viscometer.

TABLE VI. *Redwood No. 2 viscometer, temperature 70°F (corr.).*

Taken from Smooth Curve Redwood No. 2 (seconds)	Kinematic viscosity	Calculated kinematic viscosity*
32.5	0.7675	0.7682
35	0.8325	0.8318
40	0.9575	0.9582
45	1.0825	1.0838
50	1.2075	1.2090
60	1.4575	1.4583
70	1.7075	1.7067
80	1.9525	1.9539
90	2.2025	2.2023
100	2.4470	2.4470
150	3.6720	3.6710
200	4.8950	4.8940
250	6.1180	6.1170

* Calculated by formulae derived for the viscometer.

The validity of the second equation for values of T above 650 could not be investigated because the kinematic viscosities above 15.0 stokes (approximately) were outside the range of the U-tube viscometers used, but it is very probable that it may be applied to higher values than 650 seconds on this viscometer (Tables V and VI).

Apart from the parallelism between the Higgins diagrams for the No. 1 and No. 2 viscometers mentioned above, this work is interesting because it confirms an observation made by Barr[33] that the Redwood No. 2 viscometer could be used within the limits of the accuracy of timing down to times of outflow of approximately 20 seconds if the value of the constant B is approximately 0.4.

This work, however, fixes the lower limit of the useful range of the viscometer as 32 seconds (approximately). A considerable economy of time would be realized in the routine determination of Redwood times of outflow if timing errors involved during these brief determinations were small. However, any necessity for the use of this viscometer for such small times of outflow does not exist, since the Redwood No. 1 times of outflow of about 1000 seconds can be determined very accurately, so that a reasonable point for changing over from the No. 1 to the No. 2 viscometer is approximately 1000 R_1 seconds. This suggestion receives support from the fact

that timing errors involved in R_2 times of 100 seconds would not be very great.

The results reported above for the Redwood No. 2 viscometer provide means for checking the accuracy of the equation $\nu = 0.00247 \times T - 0.5/T$, which is valid for corrected or standard Redwood No. 1 times of outflow above 100.

It will be realized that when $T = 1000$, the value of the quantity $0.5/T$ is negligible (in fact, it may be ignored for all values of T greater than 300 Redwood No. 1 seconds, since by doing this, the maximum error involved is approximately 0.2 percent ($T = 300$)). Hence, this equation may be written: $\nu = 0.00247 \times T$, where T = corrected R_1 seconds above 1000.

Now, the R_2 viscometer used for this experimental work has been compared against an R_2 viscometer which had been calibrated by the N.P.L. by means of comparative flow-tests done on this instrument and the standard Redwood No. 1 viscometer, at room temperature. The correction to be applied to the instrument was found to be minus 0.8 percent. Hence, the equation $\nu = 0.02447 \times T$ for this instrument may be written as $\nu = 0.02467 \times T$. If, however, the ratio of standard Redwood No. 1 times of outflow to standard Redwood No. 2 times is 10, the value of the constant in the last equation should be 0.0247, so that there is very good agreement between both values. The equation $\nu = 0.0247 \times T$, therefore, may be used to convert *corrected* R_2 times of outflow above 100 into kinematic units.

The Saybolt Viscometers

A considerable amount of work has been done on these viscometers, and the values of the constants obtained by various workers are given in Tables VII and VIII. The most recent authoritative formulae are given by the A.P.I. Committee[4] as:

Saybolt Universal Viscometer

$\nu = 0.00226 \times T - 1.9/T$ for S_u seconds from 32 to 125

$\nu = 0.00220 \times T$ for S_u seconds above 200

Saybolt Furol Viscometers

$\nu = 0.0224 \times T - 1.9/T$ for S_F seconds from 25 to 40

$\nu = 0.0216 \times T$ for S_F seconds above 80.

It will be noticed that an intermediate range of times of outflow remains outside the scope of the formulae given for each instrument.

The data given in the tables issued by the A.P.I. Committee were employed for obtaining the Higgins diagrams curve 6, Fig. 3, for the Universal and curve 5, Fig. 2, for the Furol.

TABLE VII. *Saybolt universal viscometer.*

A	B	Reference
0.00193	1.242	Upton, Proc. A.S.T.M. **15** (i) 297 (1915). Higgins' graphical method applied to data by Waidner, ibid. Universal instruments Nos. 580 and 727.
0.0021863	1.4968	Flowers, ibid., 318. Calculated from Meissner's equations (loc. cit.) for universal viscometer No. 752.
0.00213	1.535	Herschel, Proc. A.S.T.M. **17**, 552 (1917). Bur. Standards Tech. Paper No. 100 (1917). Use of Herschel's method on viscometers Nos. 580 and 727.
0.00220	1.80	For instruments of normal dimensions: } Herschel, Proc. A.S.T.M. **18** (ii) 364 (1918).
0.00211	1.82	For instruments of minimum dimensions: } Herschel, Proc. A.S.T.M. **18** (ii) 364 (1918).
0.00230	1.79	For instruments of maximum dimensions: } Herschel, Proc. A.S.T.M. **18** (ii) 364 (1918).
0.00216	1.80	Committee D-2 A.S.T.M. Proc. A.S.T.M. **22**, 1 (1922). Deduced from average of times of flow on numerous viscometers for oil of known kinematic viscosity and on the assumption that $B = 1.80$.
0.00226	1.90	For Saybolt universal times 32 to 125 seconds. } Committee on viscosity standards of the A.R.I. (December, 1924).
0.00220	0	For Saybolt universal times over 200 seconds. } Committee on viscosity standards of the A.R.I. (December, 1924).
		Chechot, *Congrés Internationale pour l'Essai des Materiaux* (Amsterdam) **2**, 447 (1927).
Results given in present paper		
0.00226	1.95	For Saybolt universal times 32 to 145 seconds. } Deduced from the data published in the last two references.
0.00220	0.8	For Saybolt universal times over 145 seconds. } Deduced from the data published in the last two references.
0.00226	1.95	For Saybolt universal times up to 100. } A.S.T.M. D-2 Sub-committee.*
0.00220	1.30	For Saybolt universal times above 100. } A.S.T.M. D-2 Sub-committee.*

* We are informed by Dr. Delbridge that these equations are being put forward officially as suitable for the conversion of Saybolt universal seconds to kinematic viscosity. The new value for the constant B in the second equation has been based on further experimental results which were not available to us when we deduced the equations given earlier in the paper.

TABLE VIII. *Saybolt Furol viscometer.*

A	*B*	References
0.0218	1.72	Used by Danforth in *Oil Flow in Pipe Lines*, 1921.
0.0222	2.02	Herschel, Chem. Met. Eng. **26**, 1175 (1922).
0.0220	2.03	Herschel, (loc. cit.). For Saybolt Furol of standard dimensions.
0.0224	1.90	For Saybolt Furol times 25 to 40 seconds.
0.0216	0	For Saybolt Furol times above 40 seconds.
		Committee on Viscosity Standards of the A.P.I. and Chechot (loc. cit.).
Results given in present paper		
0.0224	1.84	For Saybolt Furol times 25 to 40 seconds.
0.0216	0.60	For Saybolt Furol times over 40 seconds.
		Deduced from the data given in the last two references.

TABLE IX. *Saybolt universal viscometer.*

A.P.I. Data Saybolt universal (seconds)	Kinematic viscosity	Calculated kinematic viscosity†	Percent difference	Calculated kinematic viscosity*	Percent difference
Values in italics obtained by interpolation.					
32	0.0115	0.0129	+12.6	0.0114	−1.0
40	0.0417	0.0429	+2.9	0.0416	−0.1
50	0.0740	0.0750	+1.4	0.0740	0.0
60	0.1030	0.104	+1.0	0.1031	+0.1
70	0.1300	0.1311	+0.9	0.1303	+0.3
80	0.1560	0.1570	+0.6	0.1564	+0.3
90	0.1810	0.1823	+0.6	0.1816	+0.3
100	0.2060	0.2070	+0.5	0.2065	+0.2
125	0.2660	0.2670	+0.5	0.2668	+0.3
*130**	*0.2776*	——	——	0.2788	+0.4
135	*0.2892*	——	——	0.2907	+0.5
140	*0.3008*	——	——	0.3025	+0.5
145	*0.3124*	——	——	0.3135	+0.4
150	0.3240	——	——	0.3247	+0.2
175	0.3810	——	——	0.3804	−0.2
200	0.4370	0.440	+0.7	0.4360	−0.2
225	0.4920	0.495	+0.6	0.4915	−0.1
250	0.5480	0.550	+0.4	0.5470	−0.2
275	0.6030	0.605	+0.3	0.6020	−0.2
300	0.6580	0.660	+0.3	0.657	−0.2

† Calculated by formulae given by the A.P.I. Committee on Viscosity Standards (1922–1924).

* Calculated by new Saybolt universal formulae given in this paper.

These curves also possess the characteristics of the Redwood viscometer curves and, therefore, independently confirm the observations resulting from the work described in an earlier part of the paper.

In each case, approximation curves were drawn in order to deduce equations which could be applied to *all* Saybolt Universal and Furol times of outflow. These new equations are:

Saybolt Universal Viscometer

$\nu = 0.00226 \times T - 1.95/T$ for S_u seconds from 32 to 145

$\nu = 0.00220 \times T - 0.8/T$ for S_u seconds above 145

Saybolt Furol Viscometer

$\nu = 0.224 \times T - 1.84/T$ for S_F seconds from 25 to 40

$\nu = 0.0216 \times T - 0.6/T$ for S_F seconds above 40.

These equations and those recommended by the A.P.I. Committee have been used to calculate kinematic viscosities corresponding to S_u and S_F seconds, and a comparison of these calculated values with those quoted by the A.P.I. is possible with Tables IX and X. The closer agreement attained by the use of the new equations is evident.

TABLE X. *Saybolt Furol viscometer.*

A.P.I. Data Saybolt Furol (seconds)	Kinematic viscosity	Calculated kinematic viscosity*	Percent difference	Calculated kinematic viscosity†	Percent difference
25	0.486	0.485	−0.2	0.486	−0.1
26	0.512	0.510	−0.3	0.512	−0.1
27	0.537	0.535	−0.3	0.537	0.0
28	0.562	0.560	−0.3	0.561	+0.1
29	0.586	0.585	−0.1	0.586	0.0
30	0.610	0.610	0.0	0.611	+0.1
35	0.730	0.731	+0.2	0.731	+0.2
40	0.846	0.850	+0.5	0.849	+0.4
45	0.960	——	——	0.959	−0.2
50	1.072	——	——	1.068	−0.4
60	1.292	——	——	1.296	−0.3
70	1.507	——	——	1.503	−0.2
80	*1.724*	1.728	+0.2	1.720	−0.2
90	1.939	1.944	+0.2	1.937	−0.1
100	2.155	2.160	+0.2	2.154	−0.1

* Calculated by formulae given by the A.P.I. Committee on Viscosity Standards (1922 to 1924).

† Calculated by new Saybolt Furol formulae given in this paper. The value 1.724 for the kinematic viscosity corresponding to 80 Saybolt Furol seconds is reproduced from the table given by Herschel, Int. Crit. Tab., **1** (1926), because the value 1.804 appearing in the A.P.I. report and in the paper by Chechot (loc. cit.) is given by error.

THE ENGLER VISCOMETER

In 1907, Ubbelohde[34] derived the following equation for the Engler viscometer $z = 4.072\ E^0$

[34] Ubbelohde, *Tabellen zum Englerschen Viscosimetern*, S. Hirzel, Leipzig, 1907.

TABLE XI. *Engler viscometer.*

A	*B*	Used with Engler	Reference
0.073	0.0631	Degrees	Ubbelohde, Tabellen zum Englerschen Viscosimetern, S. Hirzel, Leipzig (1907).
0.0015723	3.5767	Seconds	Meissner, Chem. Rev. Fett-Harz. Ind. **17**, 202 (1910).
0.0864	0.08	Degrees	R. v. Mises Elements der Technischen Hydromechanik, G. B. Teubner, Leipzig u. Berlin (1914).
0.001435	3.22	Seconds	Higgins, Collected Researches of the N.P.L. **11**, 14 (1914). Calculated from Ubbelohde's quotation, loc. cit.
0.001432	3.216	Seconds	Upton, Proc. A.S.T.M. **15**, (i), 296 (1915). Calculated from Waidners data, loc. cit.
0.00147	3.74	Seconds	Herschel, Proc. A.S.T.M. **17**, (ii), 562 (1917), obtained for Engler viscometer No. 2204 U (water rate 51.3 secs.).
——	——	Degrees	Vogel, Zeits. f. angew Chemie **35**, 561 (1922), suggested $v = E^0 \times 0.076^{(1-1/E^3)} \cdot f(v)$ or more simply, since $f(v)$ is practically unity, $v = E^0 \times 0.076^{(1-1/E^3)}$.
0.08297	0.0834	E′	Kirsten and Schiller, Zeits. f. ang. Math. u. Mech. **5**, 111 (1925). E′ refers to Engler degrees calculated not with the time of outflow of water at 20°C but with the "ideal" time of outflow.
Suggestions in present paper			
0.08	0.0864	Degrees	For E^0 from 1.35 to 3.20 } Based on Erk's tables.
0.076	0.04	Degrees	For E^0 over 3.20 }

$-3.518/E^0$ where z = relative viscosity (referred to water at 0°C) and E^0 = observed Engler degrees.

Hence, if one takes into account that the kinematic viscosity of water at 0°C is 0.01792, this equation can be changed into the more conventional form:

$$\nu = 0.073\,E^0 - 0.0631/E^0.$$

The accuracy of this equation was tested by Holde[35] who found that, when E^0 is above 7, the converted values were too low by about 4.2 percent, whereas for lower values of E^0 (below 5) this error was greater (about 8 percent). Later, Vogel published a more complicated conversion equation, namely: $\nu = (E^0/100) \times 7.61^{(1-1/E^3)} \times f(\nu)$ where $f(\nu)$ is a temperature function of the viscometer and which is practically equivalent to unity.

The equation in its simple form, therefore, is: $\nu = (E^0/100) \times 7.6^{(1-1/E^3)}$ which has been investigated recently by Erk[15] who concluded that it represents, better than any other equation, the relationship between kinematic viscosities and E^0 [36] (Table XI).

Table XII taken from Erk's paper gives the kinematic viscosities calculated by means of Vogel's equation to correspond to various values of E^0. These figures have been employed to give the Higgins diagram shown in Fig. 4, curve 1.

The unusual form of this curve is evident when it is compared with those given in Figs. 3, 1, 2 for the Redwood and Saybolt viscometers, which like the Engler viscometer are short-tube efflux instruments. A close examination of the curve revealed the possibility of the derivation of the following less-complicated and more-conventional

TABLE XII. *Engler viscometer.*

E^0	Kinematic Viscosity Given by Erk*	Kinematic Viscosity Calculated†	E^0	Kinematic Viscosity Given by Erk*	Kinematic Viscosity Calculated†
1.00	0.010	——	2.70	0.184	0.184
1.05	0.014	——	2.80	0.193	0.193
1.10	0.018	——	2.90	0.202	0.202
1.15	0.023	——	3.00	0.211	0.211
1.20	0.028	——	3.20	0.228	0.229
1.25	0.033	——	3.40	0.245	0.245
1.30	0.039	0.0375	3.60	0.261	0.261
1.35	0.045	0.0440	3.80	0.277	0.277
1.40	0.050	0.0503	4.00	0.293	0.293
1.45	0.056	0.0563	4.20	0.309	0.309
1.50	0.062	0.0624	4.40	0.325	0.324
1.60	0.074	0.074	4.60	0.341	0.340
1.70	0.085	0.085	4.80	0.357	0.355
1.80	0.096	0.096	5.00	0.373	0.371
1.90	0.107	0.107	5.50	0.412	0.410
2.00	0.118	0.117	6.00	0.451	0.449
2.10	0.128	0.127	6.50	0.490	0.487
2.20	0.138	0.137	7.00	0.529	0.526
2.30	0.148	0.146	7.50	0.568	0.564
2.40	0.157	0.156	8.00	0.606	0.602
2.50	0.166	0.165	10.00	0.760	0.756
2.60	0.175	0.175	20.00	1.520	1.518
			30.00	2.280	2.279

* Calculated by Vogel's Equation; values given by Erk (loc. cit.)

† Calculated by New Engler formulae given in this paper.

[35] Holde, Verhandl. der 8 Intl. Kongr. für angew. Chemie zu New York **15**, 677 (1912).

[36] Data agreeing with Vogel's equation and Table VIII have been adopted officially by the *Deutscher Verband für die Materialprüfungen der Technik*, Auschuss 9.

equations for the Engler viscometer: $\nu = 0.08 \times E^0 - 0.0864/E^0$ for E^0 between 1.35 and 3.2 (curve 2, Fig. 4); $\nu = 0.076 \times E^0 - 0.04/E^0$ for E^0 above 3.2 (curve 3, Fig. 4).

The accompanying Table XII, containing the values of ν calculated with Vogel's equation and with the two equations mentioned, shows substantially good agreement to exist between both sets.

The part of curve 1 below the value $E^0 = 1.35$ has a progressively decreasing slope which suggests that the critical velocity of outflow in the Engler instrument, from streamline flow into the unstable region leading to the establishment of turbulent flow. Various authorities differ on this point.

For instance, Herschel derived the following equation for an Engler viscometer. $\nu = 0.00147 \times T - 3.74/T$ where T is the observed Engler time and stated that the equation should not be used for values of T below 56 seconds.[37] Herschel explains the fixing of this lower limit by stating that the critical velocity of outflow occurs near to this value of T (i.e., roughly equivalent to 1.1 E^0).

Erk,[15] on the other hand, has asserted that turbulence is established at a point corresponding to a value of 0.96 E^0, the value for water between 50°C and 60°C. This conclusion is of doubtful value because in his experiments, Erk had the exit end of the Engler orifice submerged in water, whereas in practice the stream flows into the atmosphere and then into the Engler flask.

The complicated nature of Vogel's equation, therefore, is probably due to the desire to provide for small values of E^0 which fall in an unstable region of flow.

In addition, Erk[38] claims that the Engler viscometer does not require a standard tube as with the Redwood and Saybolt instruments. This claim is based on the assumptions that efflux times are influenced to the same degree, in a manner dependent on the changes in the dimensions of the apparatus and on the varying efflux time of water which is the sole means of calibration for this viscometer. Erk also suggests that in Germany uniformity is practically being obtained because no other conversion equation (than Vogel's) is frequently used.

The recently published results of Weick,[25] on the other hand, indicate that different values for Engler degrees are given for the same oils by different Engler viscometers which comply with all the dimensional requirements and the limitations on the water rate at 20°C, specified in the official German specifications for this instrument.

It appears, therefore, that uniformity in the determination of Engler degrees can be achieved as with viscometers of other types only by the calibration of all Engler viscometers by comparative flow tests against a national standard viscometer, or a generally accepted equation such as Vogel's.

Uniformity of the kinematic viscosities derived from Engler degrees will then be the natural result of the general adoption of an equation found to apply over the whole working range of the standard Engler viscometer.

[37] Both Herschel's and Vogel's equations have been quoted in the B.E.S.A. specification No. 188 (1928) on absolute viscosity determinations, as suitable for the conversion of Engler times or degrees into kinematic viscosities. Herschel's equation is no longer tenable in view of the later work of Vogel.

[38] Erk, J. Rheology **2**, 164, 165 (1931).

On the Nature of "Yield-Value"

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The problem of the *flow of materials* at stresses far below their normal yield-values is discussed, and it is pointed out that the sharpness with which yield-values can be measured depends on the grouping of the relaxation times for the different strains set up within the material, an uneven distribution making for a sharper definition. Any sharp and drastic change in the relaxation time of the system as a whole may justifiably be said to constitute a yield-value, the question as to which of these points is actually taken as *the* yield-value depending on the conditions of the experiment. These considerations are reinforced by a discussion of the results (to date) of certain experiments on flour doughs, and it is claimed that flour dough is a peculiarly suitable material for such investigations. A new rapid method for studying flow in flour doughs, recently described in the literature, is discussed. The dangers of classifying materials in hard-and-fast rheological divisions is emphasized, while it is pointed out that for practical purposes, and given adequate safeguards, such classifications may be extremely useful.

Introduction

ALTHOUGH a general idea of the distinction between fluids and solids had been in common use long before the time of Maxwell, it appears that it was he who first attempted a rigid definition. Bingham[1] quotes a passage from Maxwell's *Theory of Heat* which begins "If the form of the body is found to be permanently altered when the stress exceeds a certain value, the body is said to be soft or plastic and the state of the body when the alteration is just going to take place is called the limit of perfect elasticity. If the stress, when it is maintained constant, causes a strain or displacement in the body which increases continually with the time, the substance is said to be viscous.

"When this continuous alteration of form is only produced by stresses exceeding a certain value, the substance is called solid, however soft it may be. *When the very smallest stress, if continued long enough, will cause a constantly increasing change of form, the body must be regarded as a viscous fluid, however hard it may be.*"

This idea of a yield-value or "critical" shearing stress to be applied before any displacement will occur, has been widely extended, and, in the hands of Bingham, and later of many other workers, has yielded results which have been of great value in connection with many scientific and industrial problems.

At an early stage in these investigations, however, it became apparent that the matter was not quite as simple as Maxwell's definition would lead one to believe. Experiments were generally carried out in an apparatus of the capillary tube type, which meant that, since the critical shearing stress is not attained at all points over the cross section of the tube at the same pressure, the flow curve (flow-per-second/pressure), although linear for many systems for high pressures, shows a curving off towards the origin where the pressure is low. This was to be expected on theoretical grounds, and the equation of the curvilinear part was deduced independently by Buckingham[2] and Reiner,[3] but even this equation does not fully explain the behavior of materials, so that most investigators felt that data obtained at low pressures were unreliable, and should be discarded. Various attempts were made to improve on this very unsatisfactory state of affairs. Scott Blair and Crowther,[4] following on Buckingham's deduction concerning slip at the capillary wall, and Green's[5] preliminary tests for this phenomenon, showed that a regular slip region could be observed in the case of clay and soil pastes, and that the flow-equation in this region differed little from that of Buckingham. As a

[1] E. C. Bingham, *Fluidity and Plasticity*, p. 215, 1922.

[2] E. Buckingham, Proc. Amer. Soc. Test. Mats. **21**, 1154 (1921).

[3] M. Reiner, Kolloid Zeits. **39**, 80 (1926).

[4] G. W. Scott Blair and E. M. Crowther, J. Phys. Chem. **33**, 321 (1929).

[5] H. Green, Proc. Amer. Soc. Test. Mats. **20**, 450 (1920).

result of this work, two points were made clear: (1) for pressures below the critical for plug-flow, pastes will hold up stress without yielding for very long periods; and (2) the curvilinear portion of the flow-curve still does not follow the Buckingham-Reiner equation. The second point, leading to studies on anomalous flow in the neighborhood of the tube walls, need not be discussed further here, but the first is important for the present discussion since it shows, far more conclusively than hitherto, that suspensions of rigid particles do show true rigidity, even though the yield-value of such rigidity cannot be directly measured by the capillary tube method.[6]

Meanwhile, for technical and other purposes where simplicity of treatment was essential, it had become customary to plot the upper portion of the flow-curve only, and if this appeared to be straight, to extrapolate it to the stress axis, taking the extrapolated intercept as the yield-value, and the slope as the mobility of the system. It is clear that the term yield-value is here being used in rather a loose sense. The extrapolated intercept corresponds to a stress which, if the Buckingham-Reiner equation held, would be equal to 4/3 of the true yield-value. Actually, a value of about 3/2 has been found for soil pastes, but this figure is purely experimental, and has no theoretical foundation. Hatschek[6a] therefore, is perhaps justified in denying a physical significance to this construction. He goes on to say, however, that "it can hardly be accepted even as a geometrical method of finding a constant in possible empirical equations, for the following reason: either the curve does not actually become a straight line, in which case the choice of the straight portion is arbitrary, and a matter of scale, or else the curve at some point literally becomes a straight line which means a discontinuity or change in the type of flow. . . ." On the basis of the Buckingham-Reiner equation, however, which gives a curve which does not differ too widely from the experimental curves to invalidate the argument, it is possible to calculate the order of the errors involved in drawing the asymptote. In this way, assuming an unbroken flow-curve, Schofield and Scott Blair[7] have shown that although the drawing of the straight line is "arbitrary and a matter of scale," yet the discrepancy in flow-per-second will be less than 1 percent for values of stress greater than 2.2 times the intercept. "Above this limit, the difference between the true curve and the limiting straight line should be outside the limits of experimental error. This is borne out in practice with soil and clay pastes so that linear extrapolation appears justified with these materials."

However convenient the use of the extrapolated intercept may be, it has been found better to keep the term yield-value for the true critical shearing stress. Bingham[8] has recently defined yield-value as "The minimum shearing stress in dynes per square centimeter required to produce continuous deformation in a solid." For reasons which will be made clear in this paper, it is suggested that a slight modification should be made in this definition, so as to include as a yield-value any critical shearing stress below which no flow can be observed *under the conditions of experimentation.* (The word "solid" is perfectly correct in the sense of Maxwell's definition, but since it may be a trifle hard for some people to think of weak suspensions, etc., as solids, there is something to be said for substituting the word "pachoid."[4]) In this sense, it is possible to evaluate under normal experimental conditions, a property of pastes commonly called yield-value, which, expressed as a stress per unit area at the capillary wall (in the case of the capillary plastometer), is independent of the capillary dimensions within fairly wide limits.

It has recently been shown, however, that many materials which give a yield value, show measurable plastic flow at stresses far below their normal yield-value if the stress is applied for a long enough period of time. For example, Rosbaud and Schmid[9] and Whitby[10] have published interesting studies of the "slow yield" of rubber, and Bingham[11] faces the same difficulty

[6] Compare E. Hatschek, *The Viscosity of Liquids*, p. 215, 1928.

[6a] Reference 6, p. 209.

[7] R. K. Schofield and G. W. Scott Blair, J. Phys. Chem. **34**, 248 (1930).

[8] E. C. Bingham, J. Rheology **1**, 507 (1930).

[9] P. Rosbaud and E. Schmid, Zeits. f. tech. Physik **9**, 98 (1928).

[10] G. C. Whitby, J. Phys. Chem. **36**, 198 (1932).

[11] E. C. Bingham, J. Rheology **3**, 341, 373 (1932).

in discussing the extremely interesting phenomena described by him with regard to the slow yield of stone. He remarks that "it is a matter of considerable interest that solids like marble should show so small a yield-value."

This phenomenon of slow yield presents us with a serious problem which is being faced in different ways by a number of rheologists. Some deny any meaning to yield-value in the ordinary sense, while others prefer to regard slow yield as an altogether separate phenomenon, the flow occurring below the yield-value being considered as quite different in nature from ordinary plastic flow.

Hatschek and Jane[12] and others have shown that certain sols can support very small shearing stresses in the rotating cylinder apparatus for considerable periods, but that most, but not always the whole of this stress is dissipated on still further standing. As Hatschek remarks, it is at present quite impossible to say whether these residual stresses which the systems hold up for very long periods are of the same order as, or are in any way related to the yield-value of the Buckingham-Reiner equation for the same material.

The Relationship Between Viscous and Elastic Properties of Plastic Materials

Much confusion has been caused in the past by the very natural attempts that have been made to classify all materials into a series of rheological groups (true fluids, pseudo-plastics, plastics, solid bodies, etc.). For practical purposes, such a classification is often useful, especially as our experimental methods normally test materials for periods of time of a fairly definite order of magnitude; but in taking a longer view, one is led to conclude with the Greek philosopher, that "If you wait for long enough, anything may happen," and, one might add, "If you look quickly enough anything may happen."

The treatment which follows is based on that given in a series of papers[13] concerning experiments done in this laboratory on the elastic and plastic properties of flour doughs. When a material is strained, stresses are set up which are initially proportional to the strain, but which, in the case of a material having viscosity, gradually dissipate themselves. If the initial external strain is kept constant, Maxwell assumed that the rate of dissipation of stress would be proportional to the stress itself—i.e., the stress would fall off logarithmically with time, or

$$-dS/dt = S/t_r,$$

where $-dS/dt$ is the rate of dissipation of stress and t_r is a property known as the "relaxation-time" which, in the simple case, is a constant independent of stress or:

$$t_r = -[d(\log_e S)/dt]^{-1}.$$

If t_r is great, then the stress is dissipated slowly, but if t_r is small, then the dissipation is rapid.

In the case of true fluids, t_r has not yet been measured, the rigidity modulus being, in general, extremely high, nor can any yield-value be observed for them, though yield-values have recently been found in strong salt solutions by Scott Blair and Schofield.[14]

It must be clearly borne in mind that although the "external strain" (that is to say the actual dimensions of the strained material) is kept constant, the fact that there is a dissipation of stress must imply some readjustments within the body of the material, which may be regarded as a dissipation of "internal strains." The viscosity is taken as the ratio of the stress at any point to the rate of dissipation of strain at that point by analogy with ordinary flow.

Maxwell himself remarks that it is possible that in some bodies the relaxation time may be a function of the stress, and viewed from this angle the early experiments of Trouton[15] showed that in pitch, and similar substances, it depends also on the amount of deformation.

We thus define relaxation time in terms of rate of decay of stress, and in steady flow, the rate of decay of stress itself is proportional to the rate of change of internal shearing strain G, the proportionality constant n being the rigidity modulus. n is a third of Young's modulus Y which is easily determined for most materials. If the

[12] E. Hatschek and R. S. Jane, Kolloid Zeits. **39**, 300 (1926).

[13] R. K. Schofield and G. W. Scott Blair, Proc. Roy. Soc. (In process of publication.)

[14] G. W. Scott Blair and R. K. Schofield, Phil. Mag. **31**, 291 (1931).

[15] F. T. Trouton, Proc. Roy. Soc. **A77**, 426 (et al.) (1906).

viscosity η is defined as the ratio of S to G, we at once have a simple relationship between viscosity and relaxation time, namely: $\eta = Yt_r/3$. This definition of viscosity for all materials is probably the most satisfactory, though the value dS/dG, which has been called "pseudo-viscosity," or "stiffness" is often more useful in practice for materials showing rectilinear flow-curves which do not pass through the origin.

dS/dG changes very abruptly indeed at certain points in the flow-curve, and there is therefore often no difficulty at all in deciding at what stress measurable flow starts. Such a decision in no way denies that some very slow flow of quite a different order of magnitude may take place at considerably lower stresses, which could be followed if the stresses were applied over much longer periods of time.

One is inclined to ask whether there is any true yield-value for infinitely long times of stress-application. We are not yet in a position to answer this question. Work on sols, such as benzo-purpurin, ammonium, oleate, etc.,[12] and also on flour-doughs seems to indicate that small stresses do persist for very long periods in these materials, but one is always faced with the possibility that if the system were left still longer, even these stresses would finally disappear. There seems little evidence of plastic flow of metals under their own weight at ordinary temperatures, since coins have been preserved to us retaining their raised designs for very long periods indeed; but it is at least doubtful whether there are any *noncrystalline* materials which could really be called "solid" in accordance with Maxwell's definition given on page 113.

To substantiate these suggestions, a general description will now be given of the results of some experiments on flour-doughs which have been carried out in these laboratories.

Properties of Flour-Doughs

In an earlier paper[16] a machine (the pachimeter) was described for measuring the shearing strength (yield-value) of plastic materials under rolling, and an account of some preliminary work on flour-doughs was given. This work has since been considerably extended[13] and the machine has been improved. A photograph of the improved pachimeter is given in Fig. 1.

In this process, the yield-value is determined by rolling a small cylinder of dough between two glass plates, gradually increasing the stress by loading the upper plate until the cylinder (which for low stresses rolls as a solid) starts to lengthen and thin plastically. There is some elastic lengthening even for the smallest stresses, and in order not to confuse the two phenomena, the upper plate is lifted off the sample by means of a crank device for one complete stroke in every three. Independent experiments have shown that during this stroke the sample has time to recover completely elastically, so that if an observation taken at the end of this stroke shows a lengthening of the cylinder, this lengthening may be taken as due to plastic, as distinct from elastic deformation. It was claimed in the earlier paper that preliminary experiments showed that there was "a correlation between shearing strength and flour strength," and it was further stated that "It is not claimed that the pachimeter gives an infallible measure of flour quality, but only that the results of a small number of preliminary experiments indicate that a further study of the method for the purpose of flour testing is well worth while, especially with a view to its use as a quality control instrument in the mill." Further experiment has so far in no way changed these opinions, but it has become clear that although there is a *general* correlation between yield-value and flour "strength," it is not close enough to enable flours to be placed invariably in their correct commercial order. The reproducibility of the measurement, and the regular variation of yield-value with moisture content, temperature, age of dough, etc., has been demonstrated, and it still remains a possibility that changes in output quality in a mill would be satisfactorily indicated by a change in the pachimetric yield-value.

The properties of a dough in the proofing depend on the yield under stresses applied very slowly by the gas produced in the dough (periods of the order of half an hour), whereas the stress in the pachimeter is applied to a particular section of the dough only for a fraction of a second. It therefore seems probable that it is the slow yield which is likely to give the most valuable information about the behavior of doughs prior to

[16] G. W. Scott Blair and R. K. Schofield, J. Rheology 3, 318 (1932).

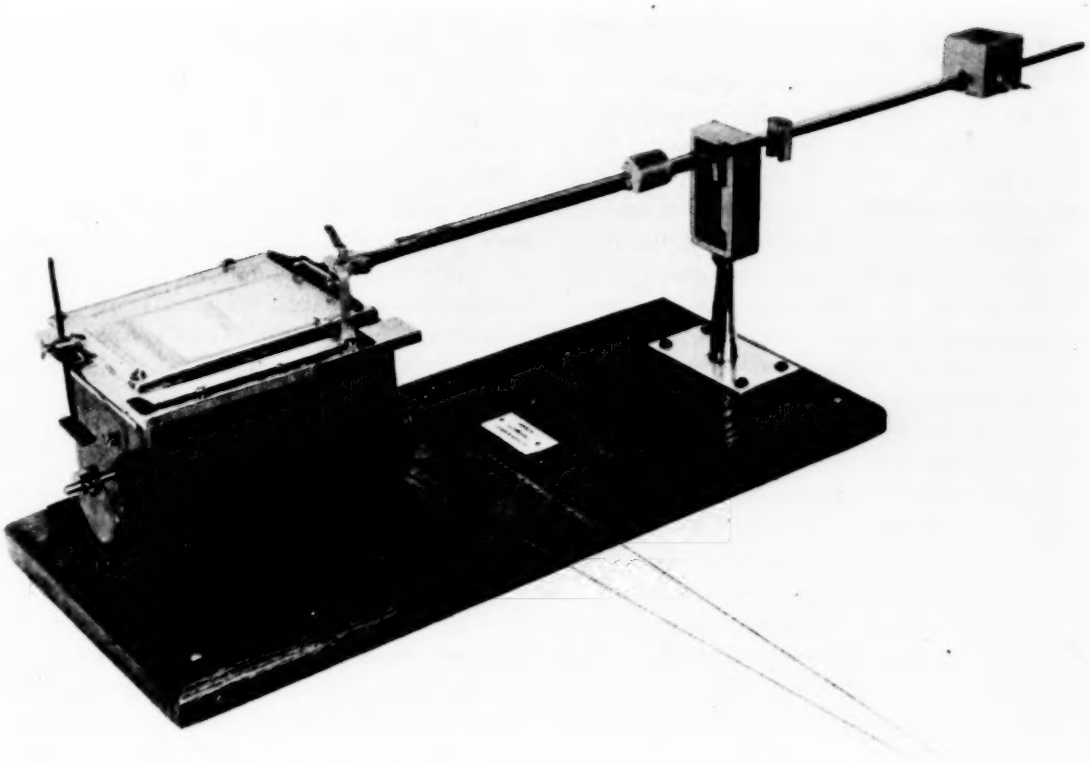

FIG. 1.

baking. A number of different methods have been used in order to obtain a measure of slow yield,[13] and it has been shown that not only is the yield-value much lower for slowly applied stresses, but that such changes as take place in the one yield-value when the dough ages, are not infrequently absent in the case of the other. For details of this work, the original papers must be consulted, but a brief outline will here be given of a very convenient method for studying slow-yield in flour doughs, which may perhaps prove useful in commercial practice as well as for scientific research.

A small cylinder of dough is prepared by forcing the dough through a narrow tube. (The dimensions of the cylinder are conveniently about 5–10 mm diameter and 10–15 cm length, though the length will depend on the nature of the flour.) The dough cylinder is hung vertically by one end in a closed test-tube over water for a convenient time (say 20 or 30 minutes), and is then removed. In order to obtain a measure of the flow which takes place, a series of parallel lines spaced 1 mm apart are marked on the dough cylinder in enamel before it is hung. This is done by means of a stamp made by wrapping a fine wire round a suitable frame. The markings neither spread nor dry, and after the flow they can be transferred to a piece of reduplicator paper. This gives a chart called a "rheogram" from which much information can be obtained; while for direct comparison of different flours, the rheograms may be compared by placing them in juxtaposition to each other. By means of this method, flow-curves can be obtained containing over a hundred points by means of a very rapid and simple experiment.*

The results of the work on flour doughs to date (October 1932) may be summarized very briefly as follows:

(1) Flour dough is found to be a very convenient material for investigating the relation-

* It is important that flours should be compared in doughs made up to the same consistency, (not necessarily the same water content). The best consistency is that at which the dough will just not stick appreciably to a glass plate when pressed firmly on to it for a moment.

ship between viscosity, elasticity and plastic strength of soft materials.

(2) The yield-values observed for flour doughs depend on the order of the time during which stresses are applied, or in other words, "the length of the time of application of a stress in relation to the corresponding time of relaxation determines what proportion of the deformation is elastic (recoverable) and what proportion plastic (non-recoverable)."

(3) Measurements have been made of the rate of decay of internal stresses in stretched doughs, and curves relating the time of relaxation (or the viscosity) to the stress have been obtained. These do not take the simple logarithmic form which would follow from Maxwell's hypothesis.

(4) The times of relaxation depend not only on stress, but also on strain. Doughs harden on working just as metals do. If flow-curves are plotted for a constant time of application of stress, they show a curvature towards the stress axis (viscosity increasing with stress) which is reminiscent of that shown by Williamson and Heckert and described by them as "inverse-plasticity."[17] There is no unique flow-curve, a series of flow-curves having been obtained for different lengths of time of stress-application.

General Conclusions

In general, it may be concluded that materials undoubtedly exist having properties in all degrees intermediate between those of a true fluid and a perfect solid. Starting from the fluid end of the scale, a number of corrections may be introduced into the Poiseuille equation to allow for the introduction of solid properties, though for any given material it will be found that certain of these corrections will be negligible by comparison with experimental error. If the flow for stresses below a certain value is very small, but increases rapidly as soon as the stress exceeds that value, this critical stress will be quite properly taken as a yield-value, although in an experiment in which much slower deformations are observable, a much lower stress would seem to mark the beginning of flow.

In view of what has been said about the relationship between viscosity and time of relaxation, the matter may be viewed from rather a different standpoint, which although it brings us to the same conclusions, in some cases makes things rather easier to visualize. We may consider the material as made up of a number of different elastic elements each having its own relaxation time. (By "element" one does not necessarily imply a particular body—a particular type of molecular linkage might constitute an element in this sense.) Although all the intermediate possibilities probably exist, it is reasonable to take three general cases. (1) All the elements have the same relaxation times. This is the case for a true fluid. The flow-curve is a straight line passing through the origin, and there is no measurable yield-value. (2) There are elements having all orders of relaxation times, fairly evenly distributed from 0 to ∞. In this case the flow-curve is curvilinear (pseudo-plastic) but it will not be possible to distinguish any yield-value. (3) There is a small number of principal groups of elements, each having its own relaxation time, but these times differ widely from group to group. These materials are true plastics. The flow-curve shows one or more sharp bends, at which the order of magnitude of the flow changes with a very small change in stress. As to which of these critical stresses is determined as the yield-value, will depend on the time during which the stresses are applied in relation to the times of relaxation of each group; in other words, on the order of magnitude of the deformations which the experimental method is designed to observe.

In some cases, it will be possible to suggest a physical interpretation for these groups of elements, as Shorter[18] and others have done, but even if this is not feasible, the author believes that he is not alone in finding this elastic model easier to visualize, than the corresponding groupings of viscosities.

Finally, it must again be emphasized that, while hard and fast divisions are often dangerous, the practical man is fully justified in differentiating between rigid and viscous resistance, and between what is, and what is not "flow," provided it is borne in mind that his differentiation is only valid under specified experimental conditions.

[17] R. V. Williamson and W. W. Heckert, Ind. Eng. Chem. **23**, 667 (1931)

[18] S. A. Shorter, J. Textile Inst. **T.15**, 207 (1924); Trans. Faraday Soc. **20**, 228 (1924); J. Soc. Dyers and Colorists **41**, 212 (1925).

Creep of Metals in Shear at High Temperatures[1]

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(Received December 9, 1931)

The properties of materials at high temperatures are receiving considerable study in the design of much industrial equipment. The present paper describes some fundamental considerations in this field by discussing the creep of metals in shear. Some theoretical and practical reasons for investigating creep in shear are given, test apparatus for this purpose is outlined, and some experimental information is included. Much more work in this type of study is desired and the paper may help to stimulate further research in this direction.

DURING recent years, particularly, there has been a growing tendency in many chemical processes and in the production and utilization of steam to increase working temperatures and the resulting pressures. For design purposes, a knowledge of the properties at high temperatures of the materials to be employed for such equipment has created a need for much study, both experimental and analytical. Still, little has been accomplished in the latter direction. The characteristic of metals gradually to change their dimensions with time under the action of temperature and stress, known as "creep," provides a very complex problem.

Just as the basis for design of apparatus at ordinary temperatures has been the tensile test, creep has been investigated in tension in order to provide data upon which to construct equipment for high temperature service. A number of considerations point to the importance of studying creep in shear for the determination of fundamental information.

It is probable that creep takes place along the shear planes and is therefore a function of the shear stress in the same manner as plastic deformation of ductile materials occurs at usual temperatures.[2] Apparently creep is present on all shear planes to a varying degree in a specimen in tension.[3] Uniformly pure shear, therefore, which is the very simplest stress condition, presents the most advantageous method for studying creep. If the maximum-shear theory is chosen as the basis of design, information of creep in shear is of direct value. Practically, creep data in shear can be obtained with far greater accuracy than in tension because, first, the effect of temperature fluctuations during tests in torsion is small and, second, much higher refinements in creep readings can be effected. In spite of the rather apparent desirabilities of studying creep in uniformly pure shear, only a very small amount of attention has been put in this direction up to the present time.[3, 4]

In the experimental program with which the author has been associated, creep of metals in uniformly pure shear is investigated by subjecting a thin tube to torsion. The specimen is twisted during any test by a known constant moment and the angular deformation measured as a function of the time. Fig. 1 shows three units for determining creep in shear. In the two units to the right, resting on the plate at the middle may be seen the automatically controlled electric furnaces which contain the tubular specimens. The torque is applied at the top. The devices for measuring shear strain are just below the centrally located plate.

The strain-measuring instruments provide four degrees of refinement. In these cases the devices are fastened to a rod and sleeve, each clamped inside the specimen. The projectors seen in the two right-hand units of Fig. 1, attached to the lower

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[1] Paper presented at the Meeting of the Society of Rheology at Rochester, New York, December 28 and 29, 1931.

[2] S. Timoshenko, *Strength of Materials*, Part II, p. 701.

[3] R. W. Bailey, *Creep of Steel under Simple and Compound Stresses*, Engineering **129** 265, 327 (1930).

[4] F. L. Everett, *Strength of Materials Subjected to Shear at High Temperatures*, Trans. A. S. M. E. **53**, 117 (1931).

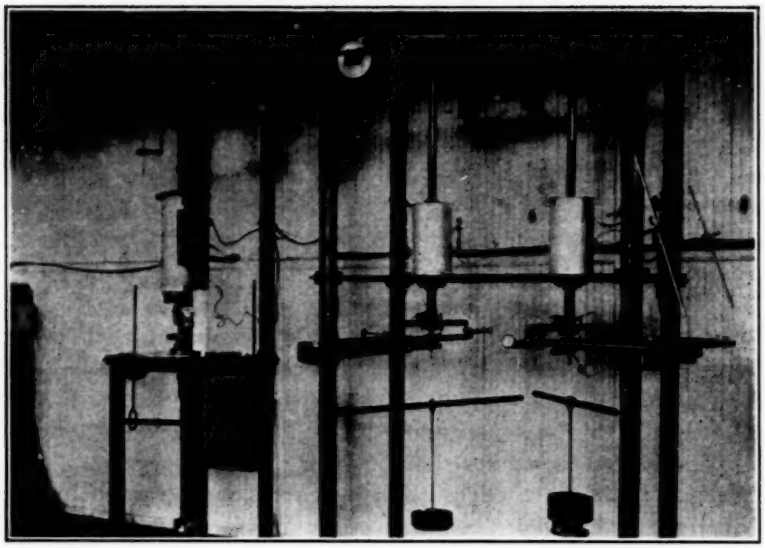
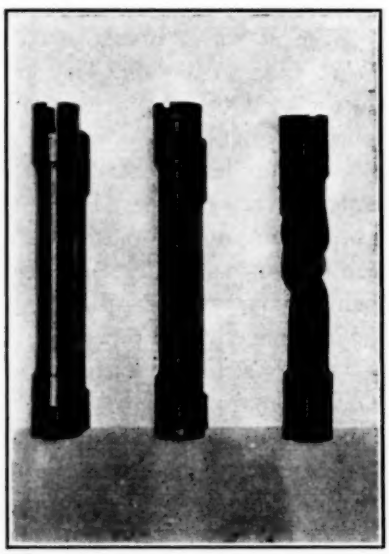


FIG. 1. Torsion units for creep of metals in shear.

ends of the rod and sleeve, cast a mark on a graduated scale which can be read as indicating a minimum rate of creep due to shearing strain of about 6×10^{-7} per hour when readings are at 12-hour intervals. The instruments which give more sensitive readings are attached to the horizontal arms. The Ames dials at the extreme right permit creep readings of 6×10^{-8}, the Huggenberger instruments at the far left, 5×10^{-9} and the Martens' mirror instruments in the middle unit, together with the telescopes and scales at the right, slightly better than 5×10^{-9} per hour, all based on readings at 12-hour periods. This latter is a refinement in detecting creep which represents the most delicate that is known to exist.



a b c

FIG. 2. Tubular specimens for creep tests in torsion. (a) Unstressed tube, (b) after creep test, (c) after buckling failure.

In the series of creep tests in shear which are described here, thin tube specimens, shown in Fig. 2a, of 0.34 C annealed steel were used. A photograph of a specimen following a creep test is given in Fig. 2b. In all cases in the creep experiments, no evidence of buckling could be observed. If angular deformations were great enough, however, buckling as illustrated in Fig. 2c could be produced and occurred with considerable suddenness.

The following experiments which serve as an example of the information which has been obtained upon creep of metals in shear, have been conducted with the apparatus outlined and upon the steel tubes at 400°C. Fig. 3 is representative of the test data taken during each creep test at constant shearing stresses. Of the three stages in each curve, the middle one is substantially of uniform slope and characterizes the minimum rate of creep. It is from this portion of the curve that values of creep, together with the corresponding shearing stress, are taken to plot the

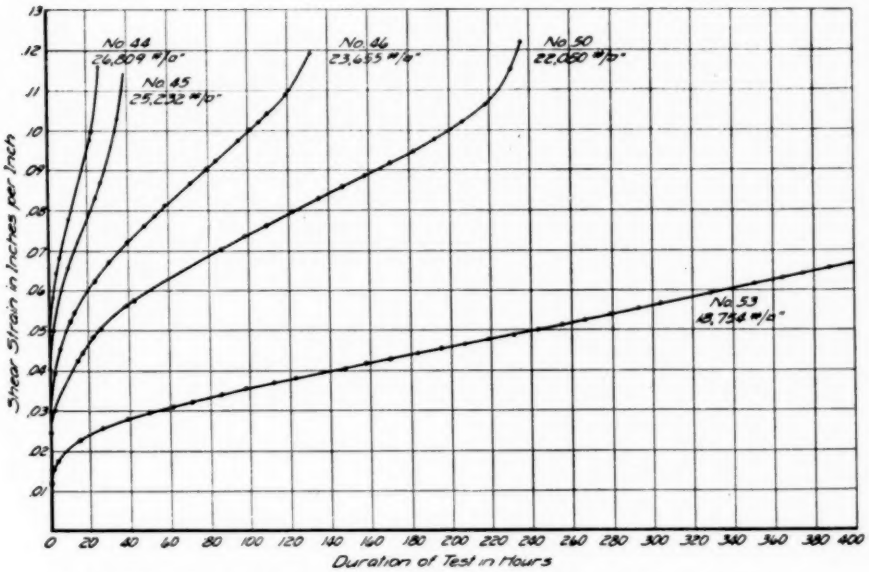


FIG. 3. Shear strain—duration of creep test in shear for various shear stresses in 0.34 C steel at 400°C.

curve of Fig. 4. The logarithmic method of plotting these creep data has been selected generally by experimenters in this field of research since over a considerable portion the curve can be considered substantially a straight line. For very low rates of creep, as can be seen in the curve, there is a noticeable rounding off, that is, at decreasing shear stresses, the minimum rates of creep decrease proportionately faster.

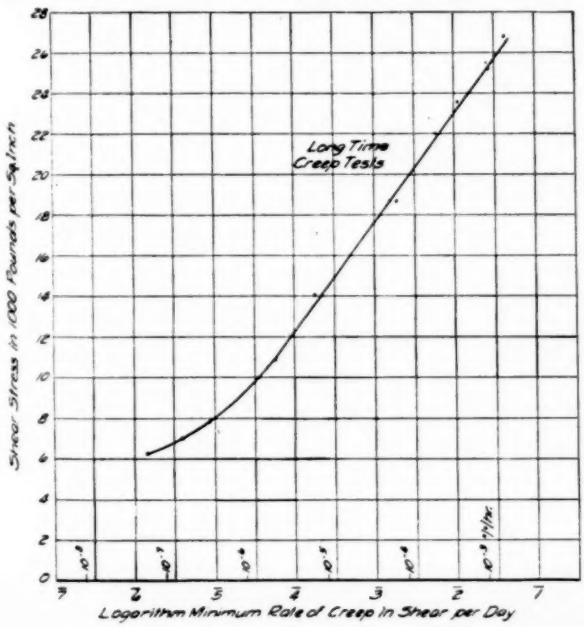


FIG. 4. Creep in shear of 0.34 C steel at 400°C.

This type of curve is of direct importance to the designer of equipment which operates at high temperatures and pressures.

Only little attempt has been made up to the present time to express creep phenomena in mathematical form. Mr. Bailey[5] and his co-authors, however, have ventured to state the relation between shearing stress f, in pounds per square inch; rate of creep in shear ϕ, in strain per hour; temperature θ, in degrees Fahrenheit; and e, the base of Napierian logarithms, as follows:

$$f=(8.7\times10^{6}/e^{0.0006\theta})(\phi/2)^{0.15}.$$

The above formula was obtained by analyzing the experimental data available to the authors. It is of interest to observe that this formula is in good agreement with the creep data reported in this paper.

This research program has had the valuable supervision of Professor S. Timoshenko in whose laboratory at the University of Michigan the work was done. The author desires to express his appreciation.

[5] R. W. Bailey, J. H. S. Dickenson, N. P. Ingles and J. L. Pearson, *The Trend of Progress in Great Britain on the Engineering Use of Metals at Elevated Temperatures*, A. S. T. M.—A. S. M. E., Symposium on Effect of Temperature on Metals, p. 218, 1931. See also discussion by author.

Simple Derivations of Some Important Relationships in Capillary Flow

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Use is made of geometrical constructions to demonstrate the conditions under which a plot of $V/\pi R^3$ against $\frac{1}{2}pR$ gives a unique curve independent of the value of R, and also to show how account can be taken of discrepancies due to modified flow near the wall of the tube. In a similar way, the reasoning from which the velocity gradient G_W at the wall of the tube can be deduced from experimental figures for V, p and R has been set out in a geometrical form, which should be helpful to those to whom a pictorial representation makes a ready appeal. The deductions, though simple, involve no loss of generality. The data of Farrow, Lowe and Neale for two percent starch paste are considered by way of example, and it is shown that their form

$$G_W = (V/\pi R^3)(N+3) \quad \text{where} \quad N = d\ (\log\ V)/d\ (\log\ p)$$

of the equation for the velocity gradient at the wall has special advantages. Later work, by disclosing a wider basis, has shown that N need not be constant as they supposed, and also that, where modified flow occurs near the wall of the tube, $V/\pi R^3$ becomes $V_\beta/\pi R^3$, the limiting value for large radii.

THE majority of rheologists are experimenters rather than mathematicians, and consequently they follow the successive steps of a reasoned deduction more readily when these are presented through the medium of diagrams than when they are represented in symbolic form. Furthermore, a geometrical figure leaves a pictorial impression on the mind, which later helps to recall the argument and the relationship to which it leads, should either be temporarily forgotten. For these reasons it is to be regretted that much of the recent development in the treatment of flow in capillary tubes has been set out by means of mathematics which, if not really difficult, take time and concentration to follow out in detail. In the following pages some of these developments are set out without any loss of generality in a way that should make them more easily seen in their true perspective.

Insofar as originality is displayed below, it is to be found in the method of deduction rather than in the results obtained. A concluding section contains a brief historical survey in which it is hoped that the various authors who have contributed to these advances receive their due portion of recognition. This section has been by no means easy to compile. The various propositions being capable of deduction *ab initio* it was to be expected that different authors would arrive at the same conclusions independently, and this has undoubtedly happened at more than one stage in the development.

THE BASIS OF THE PLOT $V/\pi R^3$ AGAINST $\frac{1}{2}pR$

In deducing the relationships which connect the volume, V, extruded per second, the pressure gradient p,* the radius of the tube R and the velocity gradient G_W at the wall of the tube, three conditions have been taken as fulfilled. (1) Each element of the flowing material moves uniformly in a straight course parallel to the wall of the tube. (2) The material in contact with the wall of the tube is at rest with respect to it. (3) The velocity gradient (or rate of shear) has one, and only one, possible value for each value of the corresponding shearing stress.

Let the curve $A_1O_1B_1$ (Fig. 1a) represent a section of a surface so constructed that it marks the position of the elements of the flowing material which one second previously were in the plane A_1B_1, and have moved forward in conformity with condition (1). Under the above conditions this surface, or extrusion, figure will be fixed when p_1 and R_1 are fixed, as will also be the volume V_1 enclosed between it and the plane A_1B_1. Furthermore, if R_1 and p_1 are changed in inverse ratio to R_2 and p_2 (Fig. 1b), so that

* It is convenient to write $p = P/L$, P being the pressure difference at the ends of a tube of length L.

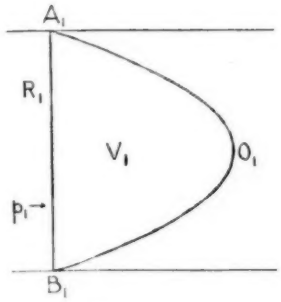

FIG. 1a.

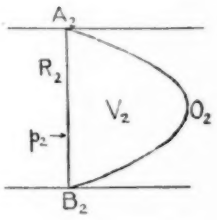

FIG. 1b.

$\frac{1}{2}p_1R_1=\frac{1}{2}p_2R_2$, and, therefore, the shearing stress at the wall is unaltered, the *scale* of the extrusion figure changes, but its *shape* will be unaffected. This follows from condition (3), since the inclination of the extrusion surface to the normal cross section at any point is the velocity gradient, and this is fixed by the shearing stress. The shearing stress in both figures increases uniformly from zero on the axis to the same value at the wall of the tube. It, therefore, follows that V, being a volume, must, if it retains its shape unaltered, vary as the cube of the radius: i.e., $V_1 : V_2$ as $R_1^3 : R_2^3$ or $V_1/\pi R_1^3 = V_2/\pi R_2^3 = K$, a constant for a given stress at the wall.

This is the essence of the reasoning which forms the basis of the practice of plotting $V/\pi R^3$ against $\frac{1}{2}pR$, when data for the variation of V with p are available for several values of R. It shows that failure of points so plotted to fall on a common curve must be due to a nonfulfillment of one or more of the three conditions set out above, and cannot be accounted for by any equation however complicated which fulfills them.

The deductions of the next section can at once be made and used when this plot indicates a fulfillment of the conditions. Cases where it shows discrepancies are considered in the section that follows it.

THE DETERMINATION OF G_W, THE VELOCITY GRADIENT CORRESPONDING TO THE STRESS AT THE WALL OF THE TUBE

Where the results of such a plot indicate fulfillment of all three conditions a further step may be taken by considering the variation of V with p when R remains unaltered. In passing from the condition represented by Fig. 2a to that in Fig. 2b, the pressure gradient rises by dp, hence the stress at the wall in Fig. 2b is greater than that in Fig. 2a. Two lines PQ and $P'Q'$ can, however, be drawn in Fig. 2b to represent an imaginary cylindrical surface coaxial with the tube over which the stress is equal to that at the wall in Fig. 2a. The distance, dx, of this surface from the wall is given by $dx/R=dp/p$, (or, in words, dx is the same fraction of R as dp is of p).

The difference between the extrusion volume represented in Fig. 2b and that in Fig. 2a may be regarded as arising from two causes:

(1) There is an additional extrusion represented in Fig. 2b by the figure $A'B'B''A''$. This is substantially cylindrical in form, since dx, although made large in the diagram for the sake of clearness, is infinitesimal by comparison with R.

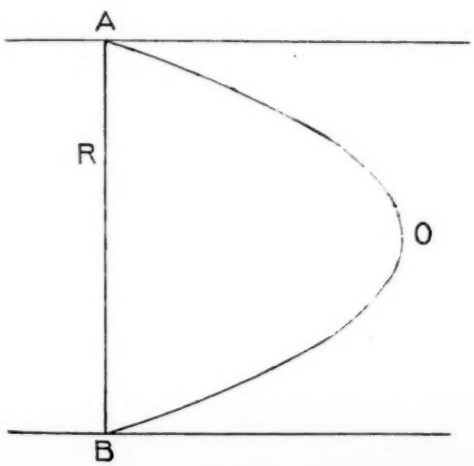

FIG. 2a.

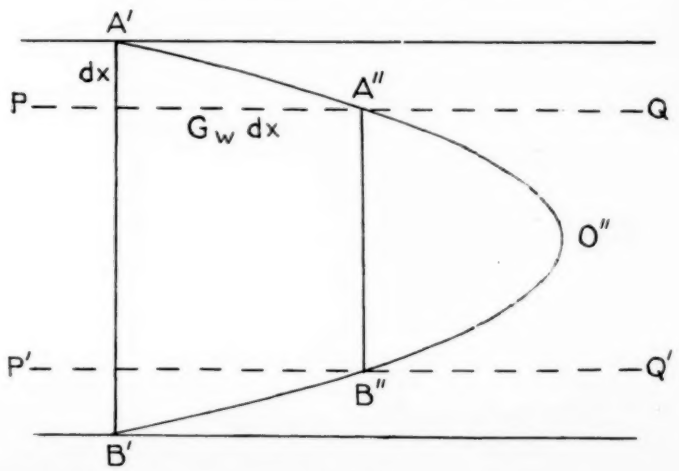

FIG. 2b.

The length of the cylinder in relation to dx (and therefore to dp) is evidently governed by the inclination of $A'A''$ to $A'B'$, which is itself a measure of the velocity gradient, G_W, at the wall of the tube. Hence this *additional* volume equals

$$\pi R^2 \cdot G_W dx = \pi R^2 \cdot G_W \cdot R(dp/p).$$

(2) The remaining volume represented by $A''O''B''$ has, according to the principle developed above, the same *shape* as that represented by AOB since the shearing stress at A'' and B'' equals that at A and B. It has, however, suffered a fractional diminution which is three times that of its linear dimensions, so that *diminution* in this remainder equals $3V(dx/R) = 3V(dp/p)$. The net change, dV, is therefore

$$dV = \pi R^3 G_W(dp/p) - 3V(dp/p).$$

In order to show how this expression can be used, it is convenient to consider an imaginary case of some data in which a plot of $V/\pi R^3$ against $\frac{1}{2}pR$ leads to the curve DE (Fig. 3). It is, of course, presumed, in accordance with the principle set out in the previous section, that capillaries have been used covering a wide range of radii, and that all the points fall close to this curve. The expression above for dV can be recast by simple algebraic rearrangement into the form

$$G_W = 3(V/\pi R^3) + \tfrac{1}{2}pR \cdot d(V/\pi R^3)/d(\tfrac{1}{2}pR).$$

Consider a point L on the curve. The first term is equal to three times OM, while the second is given by MN, since $d(V/\pi R^3)/d(\frac{1}{2}pR)$ is the slope of the tangent LN. Hence for the point L

$$G_W = 3OM + MN = 4OM + ON.$$

G_W would equal $4OM$ if Poiseuille's law were obeyed, so that ON is a measure of the departure. The importance of this construction (or any equivalent computation) is not merely that it enables a determination to be made of the velocity gradient at the wall of the tube. By condition (3) the velocity gradient is determined solely by the corresponding shearing stress; hence in G_W we have the velocity gradient which would correspond to the stress $\frac{1}{2}pR$ wherever it may occur. A plot or tabulation of G_W against $\frac{1}{2}pR$ gives all the information needed to characterize the flow of a material which conforms to the three fundamental conditions.

Before discussing in more detail this way of determining G_W, it is desirable to consider one cause of breakdown of condition (3) which is very common and which leads to discrepancies when the $V/\pi R^3$ test is applied.

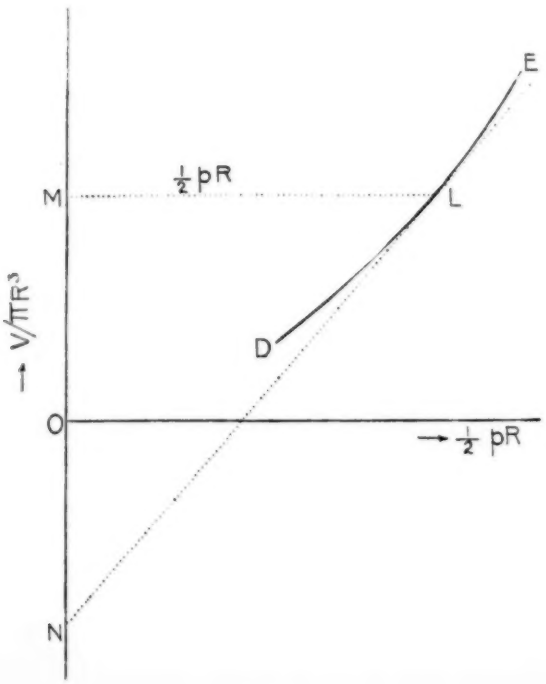

FIG. 3.

BREAKDOWN OF THE $V/\pi R^3$ TEST BECAUSE OF MODIFIED FLOW CLOSE TO THE WALL OF THE TUBE

It appears in these cases that, in a region close to the wall of the tube, the velocity gradient depends on the proximity of the wall, as well as on the shearing stress. Fig. 4a depicts a condition similar to that in Fig. 1a except that condition (3) is only fulfilled inside a cylindrical surface distant e from the wall of the tube. From its apex at O_1 to the circle in which it cuts this cylindrical surface, which is represented by the points Y_1 and Z_1, the extrusion figure follows the same course as in Fig. 1a. Between the cylindrical surface and the wall, however, it departs progressively from it, and meets the wall at C_1D_1 and not at A_1B_1.

Confining our attention to the case in which the distance e is sufficiently small in comparison with R for the stress within it to be sensibly constant, we must visualize a region in which the

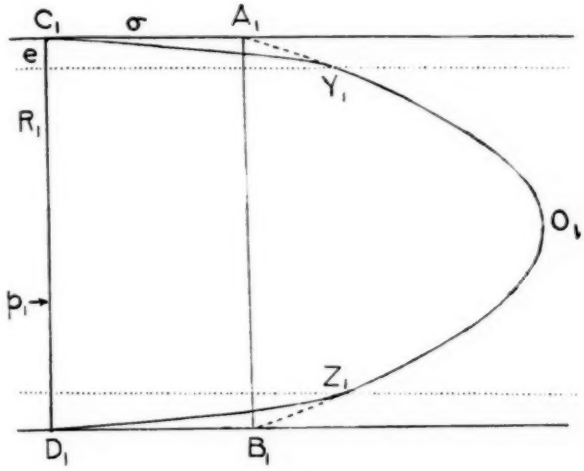

FIG. 4a.

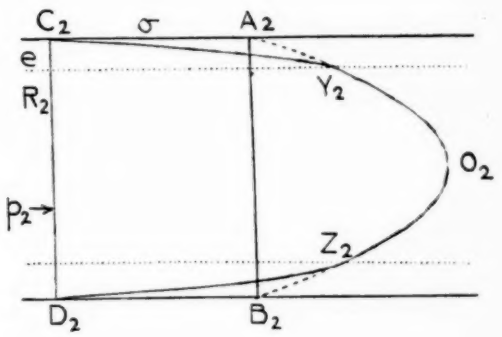

FIG. 4b.

velocity gradient steadily increases as the wall is approached because of some modification of the properties of the material. On this view the velocity gradient, represented by the inclination of any section of the curve Y_1C_1, is controlled almost entirely by its distance from the wall, and scarcely at all by the radius of the tube; from which it follows that C_2Y_2 of Fig. 2b follows the same course as C_1Y_1, and hence that $C_1A_1 = C_2A_2 = \sigma$. σ is the extra velocity with which all the material in the center of the tube is moving as a result of this effect which, until its physical basis is better understood, may conveniently be spoken of as the σ-effect.

When this effect is present, the volume V extruded in unit time through a tube of radius R may, without sensible loss of exactness, be expressed as a sum, thus $V = V_\beta + V_\sigma$. V_β, represented by the figure $A_1O_1B_1$ or $A_2O_2B_2$, is the extrusion that would have occurred had the properties possessed by the material in bulk been unaffected by the presence of the wall, so that since

$$V_\beta/\pi R^3 = K; \quad V_\beta = \pi R^3 K.$$

V_σ is represented by $C_1D_1B_1A_1$ or $C_2D_2B_2A_2$, hence $V_\sigma = \pi R^2\sigma$. The volume represented by $A_1Y_1C_1$ and $B_1Z_1D_1$, being of second order, is neglected. We may therefore write either

$$V/\pi R^2 = R \cdot K + \sigma$$

or

$$V/\pi R^3 = K + \sigma(1/R) = V_\beta/\pi R^3 + \sigma(1/R)$$

so that K and σ may be found either by plotting $V/\pi R^2$ for a constant value of $\frac{1}{2}pR$ against R, or the corresponding $V/\pi R^3$ against $1/R$ whichever seems more convenient. The expression for $V/\pi R^2$ has the more obvious physical meaning, since this is the mean velocity which is increased by a constant amount due to the σ-effect. $K = V_\beta/\pi R^3$ is, on the other hand, the limiting value which $V/\pi R^3$ approaches as R increases, and is the quantity that must be used in calculating the value of G_W corresponding to a stress $\frac{1}{2}pR$ *in the bulk of the material.*

PRACTICAL METHODS OF EVALUATING G_W

Having digressed in order to show that the construction in Fig. 3, although evolved in the first instance for use in cases where all of the three fundamental conditions are fulfilled, has in fact a wider application, we may now return and consider it further. It is clear in general that the accuracy of the results obtained by using it (or any equivalent calculation) will depend on the degree of certainty with which the tangent at L can be drawn (or computed). Where DE appears to be straight, the determination is simple. Even when it is curved, G_W can still be obtained without much difficulty if the form of the curve is known (even empirically); for then a straight line can be obtained by a suitable plot. If, for instance, a plot of log $V/\pi R^3$ against log $\frac{1}{2}pR$ conforms within the limits of experimental error to a straight line, use may be made of this fact.

If we write $N=(d \log V/\pi R^3)/(d \log \frac{1}{2}pR)$ $(=d \log V/d \log p$ for any single value of $R)$ for the slope of this line, the expression for G_W becomes

$$G_W=(V/\pi R^3)(3+N)=4(V/\pi R^3)+(N-1)V/\pi R^3,$$

so that ON is, in this case, directly proportional to $V/\pi R^3$.

Where a direct plot of $V/\pi R^3$ against $\frac{1}{2}pR$ appears to be straight, on extending it far enough into the region of low stresses, a curvature is invariably to be found. ON in this case is practically constant over the higher stresses, but starts to diminish when the stress is sufficiently reduced. On the other hand, when data for a limited stress range seem to give a straight line on a log-log basis, departure is always to be found on sufficiently increasing the stress, in the sense that ON increases less rapidly than $V/\pi R^3$.

The present discussion is not concerned with *why* one or other of these plots appears under certain conditions to give a straight line. It is merely pointed out that if, with a particular set of data, the scatter of the experimental points completely masks any small curvature that may actually exist, there is no better way of determining G_W than to draw the best straight line, and use it to obtain either the intercept ON or the factor N, as the case may be.

The obtaining of such straight lines is, in general, due to the limitations of experiment rather than to the regularities of nature. In the great majority of cases, ON is neither truly constant nor varies as rapidly as $V/\pi R^3$, and the strength of the method of approach under consideration is that the circumstance presents no fundamental obstacle. There is, nevertheless, some practical difficulty in obtaining the most probable values for G_W.

Of the methods available, that of determining a series of values of $N=\Delta \log V/\Delta \log p$ between successive values of V and p for each tube has special advantages. Where the curve of $V/\pi R^3$ against $\frac{1}{2}pR$ is nearly straight, use can be made of the fact when plotting N or $N-1$ for, in such a case, since

$$ON=(N-1)(V/\pi R^3) \text{ is constant,}$$

$N-1$ plotted against $\pi R^3/V$ should give a straight line through the origin. Furthermore, where $V/\pi R^3$ needs a small correction to allow for modified flow near the wall of the tube, this scarcely affects $\Delta \log V$, since, as a close approximation, the correction takes the form of a *proportional* change; so that the uncorrected values can be used for finding N, and all the points plotted on the same curve. These points are made clearer by taking a concrete instance.

In obtaining their data for two percent starch paste, Farrow, Lowe and Neale used four capillaries of radii 0.0861, 0.089, 0.0566 and 0.0370. By plotting $V/\pi R^3$ against $\frac{1}{2}pR$, excellent agreement is found between the points for the second and third radii. Those for 0.037 fall some seven percent higher, while those for 0.086 insofar as they deviate at all, fall never more than three percent below. The deviation is small, and it is difficult to decide whether it indicates a slight modification of the material in the immediate vicinity of the wall of the tube, involving a small departure from condition (3) in that neighborhood or whether there were small inaccuracies in the determination of the radii. If we adopt the first alternative, it would appear that corrections of approximately the following amounts must be applied to $V/\pi R^3$ to obtain $V_\beta/\pi R^3$:

0.0861	5 percent,
0.089	
0.0566	8 percent,
0.0370	13 percent.

In Fig. 5 $(N-1)$ has been plotted against $\pi R^3/V_\beta$, the origin being placed on the right so that the rate of shear increases from left to right. As some of the chords connecting consecutive points on the log $V-\log p$ curves are rather short $\Delta \log V/\Delta \log p$ has been calculated between alternate determinations. The two points on the extreme left are the only ones which refer to chords between neighboring points. Each value of $\Delta \log V/\Delta \log p$ computed direct from the table of data is plotted against the geometric mean of the corresponding values of $\pi R^3/V$ to which the appropriate percentage correction has been applied to obtain $\pi R^3/V_\beta$.

Of the nineteen chords represented, fifteen slopes taken as they stand would lead to values for G_W within $\frac{1}{2}$ percent of that to be obtained by using the smooth curve. Two show discrepancies

of 1 percent, one of 2 percent, and one of $3\frac{1}{2}$ percent. The departure can in all cases be accounted for if an error of 0.5 sec. could have occurred in determining the time of flow of the measured volume.

Notwithstanding a certain amount of scatter (which, in view of the openness of the scale, is, on the whole, remarkably small), it may confidently be asserted that $N-1$ is not constant but decreases as the rate of shear increases. The data for high rates are scanty but are at any rate not at variance with the view that in this region the curve is bending round and making for the origin.

G_W is best calculated from the relationship

$$G_W=(V_\beta/\pi R^3)\{4+(N-1)\},$$

the appropriate value of $(N-1)$ being read from the curve at the corresponding value of $\pi R^3/V_\beta$. The values so obtained do not differ greatly from those given by Farrow, Lowe and Neale, since, although they used a constant value of 0.4 for $(N-1)$ which is rather high of the mean, they did not make a percentage deduction from $V/\pi R^3$ to allow for anomalous flow at the wall, and the two corrections are of the same order and in opposite senses.

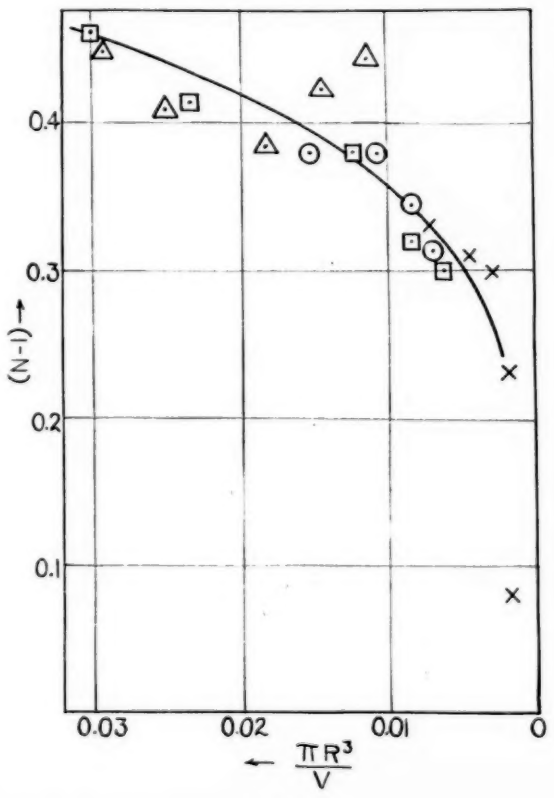

FIG. 5.

The greatest uncertainty (amounting to several percent) arises from the difficulty of making accurate allowance for the σ-effect. This uncertainty would affect the absolute magnitude of G_W rather than the manner of its variation with stress, so that it would not greatly hinder efforts to determine whether a proposed relationship between G_W and shearing stress were of the right form. A convenient way of making such a test might be to evaluate $(N-1)$ from an algebraic transformation of the proposed relationship, and see how it fits the points on Fig. 5.

There is a point of interest that is worth mentioning before leaving Fig. 5. Farrow, Lowe and Neale assumed a constant value for the slope of the line connecting log rate of shear with log shearing stress which in this case is equal to the slope N of the log V/log p curve already considered. When N is not constant, the slopes of the two curves are not strictly the same but are easily shown to be related thus

$$d\log G/d\log S=N+d\log(N+3)/d\log S.$$

In Fig. 5 the second term has a value of less than 0.02 over most of the range and is therefore of the same order as the experimental uncertainty in determining N. It is of interest, therefore, to note that the values of $d\log G/d\log S$ at low rates of shear, calculated from measurements with a Couette viscometer *rise* with increasing shear rate.

$\Delta\log G/\Delta\log S$	1.26	1.36	1.44	1.46	1.50	1.59
mean G	0.10	0.22	0.39	0.63	0.97	1.41

At high rates of shear, N falls with increasing stress, while $\Delta\log G/\Delta\log S$, calculated between the highest stress in the Couette and the lowest in the capillary viscometer, gives a value 1.57. It seems that two percent starch paste exhibits a maximum departure from the Poiseuille's law at a stress of about 10 dynes/cm^2 and a rate of shear of about 10 sec.$^{-1}$, conforming more to it, not only as the stress is increased above this (as is usually the case), but also as it is diminished below it.

Historical Development

With regard to the historical development of the ideas presented above, it is clear that the advantages of the $V/\pi R^3$ plot have been realized for a long time. Moreover, Helmholtz[1] pointed out that a slip at the wall would introduce a V/R^2 term. Appreciation of the possible disturbing effect of a wall was also shown by Reiger[2] and Glaser.[3] Green[4] demonstrated experimentally a condition (often spoken of as "plug-flow") in which shearing is confined to a very thin layer of material next the wall, and a term for this was included by Buckingham[5] in his well-known equation. The more general case, where modified flow at the wall occurs simultaneously with streamline shearing in the body of the material, was tackled by Schofield and Scott Blair[6] who showed by general reasoning that the discrepancies in the $V/\pi R^3$ plot could only be due to a departure from one of the three conditions quoted earlier in this paper. In a further paper[7] these authors showed that even when the modified layer extends to an appreciable depth from the wall the practice of plotting $V/\pi R^2$ against R and drawing the best straight line is valid within the limits of experimental error. Reiner[8] independently gives a less general consideration to the same problem. The alternative method of plotting $V/\pi R^3$ against $1/R$, which was used by Mooney[9] was considered by Schofield and Scott Blair[10] to be less suitable for the particular data under consideration, as it tended to magnify the experimental uncertainties, while the method they originally adopted tended to smooth them out. The difference between the two treatments is essentially one of expediency.

[1] Helmholtz, Wissens. Abt. Phys.-Tech. Reichsanst. **1**, 158 (1896).

[2] Reiger, Ann. d. Physik **19**, 985 (1906).

[3] Glaser, Ann. d. Physik **22**, 694 (1907).

[4] Green, Proc. Amer. Soc. Test. Mat. **20**, 450 (1920).

[5] Buckingham, Proc. Amer. Soc. Test. Mat. **21**, 1154 (1921).

[6] Schofield and Scott Blair, J. Phys. Chem. **34**, 248 (1930).

[7] Idem, J. Phys. Chem. **35**, 1212 (1931).

[8] Reiner, J. Rheology **2**, 337 (1931).

[9] Mooney, J. Rheology **2**, 210 (1931).

[10] Schofield and Scott Blair, J. Rheology **2**, 451 (1931).

Farrow, Lowe and Neale[11] appear to have been the first to attempt to calculate the relationship between rate of shear and shearing stress direct by experimental measurements in the capillary viscometer. The relationship they proposed is substantially that recommended above, except that they assumed N to be a constant, whereas in general this must be regarded as variable. Essentially similar considerations were later advanced by de Waele and Lewis,[12] Porter and Rao[13] having previously shown that a logarithm relationship between flow and pressure would arise from a similar connection between velocity gradient and stress. The more general approach emerged incidentally in a paper by Rabinowitsch,[14] but this author appeared so far unconscious of its value that he did not quote it in his summary, and it was left to Mooney[9] to emphasize its importance. Neither author makes clear the essential conditions underlying the treatment, which are those set out by Schofield and Scott Blair[6] who, as a matter of fact, gave an expression for the rate of flow in terms of the velocity gradient, which only requires an algebraic transformation to obtain the required expression.[15] In these circumstances, it seems fairest to continue to attach the names of Farrow, Lowe and Neale to the equation $G_W=(V/\pi R^3)(N+3)$, and admit that the several authors mentioned above have all contributed a share towards placing this equation on a more general footing.

[11] Farrow, Lowe and Neale, J. Textile Inst. **19**, T.18 (1928).

[12] de Waele and Lewis, Kolloid Zeits. **48**, 126 (1929).

[13] Porter and Rao, Trans. Faraday Soc. **23**, 311 (1927).

[14] Rabinowitsch, Zeits. f. physik. Chemie **145**, 1 (1929).

[15] From their equation

$$V=\frac{\pi R^3}{W^3}\int_0^W S\left\{\int_S^W 2f(S)dS\right\}dS$$

by differentiation

$$\frac{dV}{dW}=\frac{\pi R^3}{W^3}\cdot\frac{d}{dW}\left[\int_0^W S\left\{\int_S^W 2f(S)dS\right\}dS\right]$$

$$-\frac{3\pi R^3}{W^4}\int_0^W S\left\{\int_S^W 2f(S)dS\right\}dS=\frac{\pi R^3}{W}f(W)-\frac{3V}{W}.$$

$f(W)$ is what has above been called G_W and $W=\frac{1}{2}pR$; the rest is simple.